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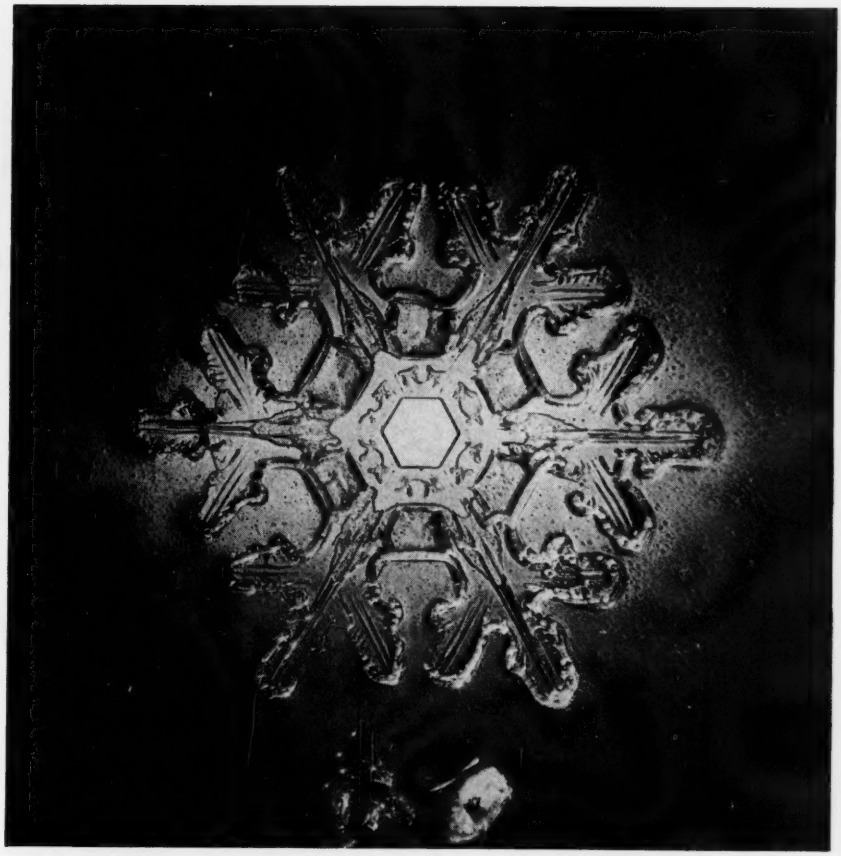

A Plastic Cast of a Snowflake

(For further information, see "From Snowflakes to Metal Surfaces," on page 348.)

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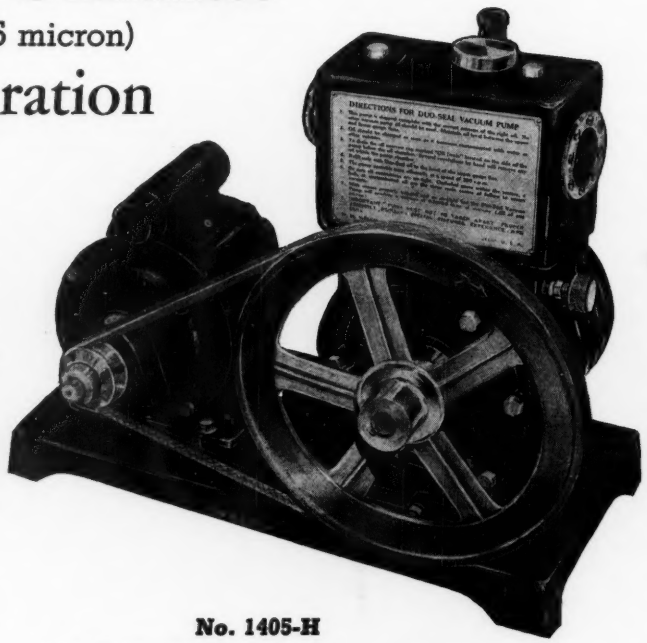

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Editor's Outlook

ONE of the most promising developments on the domestic warfront is the establishment of the Manpower Commission and its emergence as a really potent factor in the solution of a number of critical employment and labor problems. Its activities will eventually affect every teacher and university professor and every student from elementary school upwards. It will result in the expansion of vocational training facilities on a scale hitherto unknown in any country in the world. It is apparently the only means by which we can hope to clear up a lot of the present difficulties in the engineering, chemical, and general technical professions. We may see an end to the unrestricted competition between army, navy, and industry for the limited number of technically trained men; the mysteries and inconsistencies of Selective Service may become at least understandable and therefore less fearsome; our young graduates may be able to take a job with some assurance that they will be left in it and that it is a form of service to the nation of which they may be proud. It will also probably result in the enlargement of the opportunity for trained women in industry and the professions.

The competition between the armed services and industry is becoming pretty one-sided. It scarcely looks as though industry will get many of the young chemists as they come out of college. As it is now, many of them will already be committed to the army, navy, or air forces by the time they reach graduation. Each of these branches has now organized an "enlisted reserve" in which a student may enrol at the beginning of his college course, and be allowed to complete his training (presumably!) before going into active service. It is an attractive proposal and easy to sell to the young student. It makes him feel that he is in the army or navy—as indeed he is—and at the same time allows him to finish college. The advantage to the services is of course that it provides a reservoir of suitable officer material three or four years from now.

But there are some curious inconsistencies in the whole matter. Selective Service has been cracking down on occupational deferments of younger men on the plea of the urgent need for more men in the army. It has even been hinted that in order to supply the necessary several millions of men industry may possibly lose all its young men who are physically fit. The argument seems to be that any man will be more valuable with a gun in his hand tomorrow than with a wrench or test tube two years from now. It sounds more like a gambler's chance than a good insurance policy.

And that is not the way the armed services are thinking when they provide college courses for an enlisted reserve. They, at least, are not planning to use up all the ammunition in 1942, but are thinking of their needs in 1944 and 1945.

It all comes back to the same old question: whether particular, trained men are more valuable to the national service in industry or in the armed services. Let us hope that Selective Service will continue to devote itself to that problem and that the new Manpower Commission will contrive to make the selection more efficient and to allocate a suitable proportion of the technically trained men to industry, instead of allowing them to be drawn into services in which their training is only of incidental value.

All indications show that industry needs a continuous supply of young chemists, and this is more than ever true in the present time of rapid expansion for war production. If this supply is being critically depleted industry has itself partly to blame. We need to recognize that in *this* war industry is the fourth branch of the armed forces. The other branches have been doing plenty of howling for the technical men they want: So many thousands of physicists needed for the signal corps; more thousands needed for the navy; more thousands for the air corps. Why doesn't industry set up a bit of a howl, loud enough to be heard, instead of letting some of its most valuable technicians be stolen from it with scarcely a complaint? Surely, the voice of industry is powerful enough, in this country and at this time, to command respect.

All this builds up a vicious circle: the worse the situation gets the more it affects student thinking and morale, which in turn cuts down the original supply of chemists. Like the cycle of inflation it must be broken by some agency with power to enforce orders. We hope the Manpower Commission can do it.

AND speaking of howling, D. B. Keyes, in a rousing speech at the Memphis meeting of the A. C. S., expressed surprise that he hadn't heard more of it from chemists over the priorities situation concerning laboratory supplies. Declaring that he knew that chemists could howl about everything else, he wondered why they hadn't howled about *this*. A special session was devoted to considering this question which has been an acute one for some time. Representatives of supply houses pointed out that their individual firms would be able to survive by conversion to war production, even if laboratory supply business dwindled to nothing; educational institutions and other laboratories, however, would be the losers. Questions were raised, but no one seemed to know the answers, not even the men from Washington—perhaps they least of all.

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What's Been Going On

Editor's Note: While this department is generally devoted to the "goings on" in science and technology, we think that the following report, prepared by Dr. C. S. Marsh, Vice-President of the American Council on Education, deserves to be featured this month.

AT THE request of the National Resources Planning Board, and the National Roster of Scientific and Specialized Personnel, the American Council on Education has made a survey of the institutions of higher learning in order to estimate the supply of professionally trained manpower that would become available during 1942, or by early January, 1943.

Four questionnaires were sent to the institutions, asking for (1) an estimate of the number of undergraduate students who will be graduated during the year trained for 103 occupations listed by the Roster, (2) an estimate of the number of graduate students who would become available for full-time employment in the same occupations during the year; (3) an estimate of the shortage or surplus of professional manpower in teaching, research, and administrative staffs of colleges and universities, especially those qualified for certain occupations; (4) a listing of the special facilities of the institutions for instruction in subjects related to war.

The list of 103 occupations had been designated by the National Roster. These occupations were separated into seven areas: management and administration; agriculture and biology; medicine and related fields; engineering and physical sciences; social sciences; arts and languages; and clergy. While the occupations did not closely parallel the courses of study carried forward in the institutions, administrative heads were able to place most of their students within the established areas.

Nine hundred and twenty-one colleges and universities, professional and technological schools, and teacher-training institutions responded. All are institutions granting baccalaureate or higher degrees. Of this number, 812 supplied usable data. The data provide a fairly accurate estimate of the professionally trained manpower to be released this year by the institutions of higher learning.

In these institutions there will be at least *172,000 young men and women* who will become available for employment by January, 1943. Of this group, *145,000 will be graduates*, and *27,000 post-graduate students*. Many of the latter group will hold Master's degrees, and some will have their doctorates.

Colleges have compacted their courses; one technological school is delivering to industry twice its usual number of trained youth *in 16 months less time*. The three-term collegiate year is being substituted for the semester system. Vacations are being shortened, and in some schools dropped completely. Graduation exercises are at least one month earlier in the majority of institutions.

Because of these changes, young people are becoming available for employment at a steadier rate during the year. June is still the preferred graduation month, but there will be a more even flow of professionally trained persons from the colleges to industry or to the government than heretofore. The colleges estimated their students would complete their courses in the following tempo: February or March, 12,000; April or May, 43,000; June or July, 74,000; August or September, 13,000; December, 1942, or January, 1943, 29,000.

The institutions are eager to assist with the war effort. Many have night classes in the ESMDT—Engineering, Science, and Management Defense Training—courses administered by the U. S. Office of Education. Others have turned over dormitories and classrooms for use as barracks and training centers for Army and Navy fliers. Faculty members have been loaned to the government and to industry. Laboratories have been turned over to government for use in military research. Special courses bearing on actual war problems, *i. e.*, camouflage, explosives, tactics, map-making, radio communication, cryptography, military law, have been organized.

Of the *colleges and universities reporting, 95 per cent can expand their enrolments. Only 35 institutions say they definitely cannot increase enrolments;* of these, four are religious institutions (one is a Quaker school), two have sufficient equipment and staff but no housing facilities, and one has already been taken over by the Navy. *But a majority of the schools which can expand enrolments cannot expand in the subject fields in which the greatest shortage of manpower is developing. Half could expand in chemistry, but only 16 per cent could take additional students in engineering.* Twenty-five per cent could manage an increase in management and administration (New York University alone could undertake the training of 6000 additional students in this field), but less than 25 per cent of the medical schools could undertake immediate expansion.

Yet enrolments are dropping steadily. The decrease ranges from eight to twenty-five per cent among the various types of institutions. Undergraduates are entering the armed services, and also being attracted by high wages into industry. Moreover, thousands of young men and young women who might have entered college are taking jobs instead, attracted by the same high wages. Enrolments have decreased sharply in the liberal arts colleges, the teacher-training institutions, and law schools.

Few of the institutions cared to estimate their faculty shortages through 1942. Colleges report their greatest shortage in qualified personnel among men; of one group of estimated vacancies before 1943, only one-third could be filled by qualified women, in the opinion of the administrative heads of the institutions.

If such counterbalance occurs, it may not serve the best interests of the nation. *Faculty members most needed by industry, for instance, are those engaged in teaching physical sciences.* These same teachers are also the most necessary to the institutions who must train the youth demanded by industry. Moreover, research in the military problems is being carried on within the laboratories of many of the institutions. These projects, many of highly secret nature, further draw the skilled scientists out of the teaching field. In some universities, the teaching time of the scientific staffs has been cut in half by the necessary hours spent at research. It cannot therefore be said that the shortage of staffs created by the withdrawal of these faculty members will counterbalance the drop in numbers of music students, for example.

On the other hand, the youth most qualified for higher education in those sciences most necessary to a nation at war, are frequently going directly from secondary schools into industry. The nation, therefore, never has the opportunity to train some of its best talent. Moreover, college students are not only drafted off for service in armed forces, but they are tempted away by industrial wages before they have established their competence in chosen professions.

Short of actual regimentation, it might seem that nothing can be done to offset these trends. Yet the colleges themselves, with the assistance of the federal government, can make adjustments that will exercise some control on the direction of students into higher education.

Some suggested steps are:

1. *Standardization of Selective Service deferments for training in certain occupations.* In the last World War, only medical and dental students were deferred or excused from military service. In this conflict it may become necessary to defer those in training for many other occupational fields. This is a war of microscopes, and drafting rooms, and test tubes. To date the Selective Service Boards have been fairly lenient in granting deferments for youth in higher education, but no doubt better use of the facilities of colleges and universities could be made if some national policy of occupational training deferments were stated. To date, fewer than 30 medical students have been drafted in the nation; but the drafting of students in other equally needed professions has

(*Continued on page 326.*)

History of Chemistry in Louisiana

The Development of the Sugar Cane Industry[1]

E. A. FIEGER *Louisiana State University, Baton Rouge, Louisiana*

AFTER a careful consideration of the chemical developments which have occurred in Louisiana, it seemed appropriate to present the history of one of the first chemical industries of the state and to show how its introduction led to a series of developments which had far-reaching effects. This industry, which incidentally mainly concerns agriculture, was born during a period of agricultural adversity. It developed and flourished, due to the application, diligence, and patience of a small group of men who probably unconsciously applied chemical principles to a crystallization process and as so often happens, this industry in the main was content with its condition and with the results it was obtaining until the pressure of competition from an allied industry, which had enlisted the aid of scientists, caused an awakening—and its salvation through the use of chemists and engineers. This is the story of the sugar cane industry.

If history is correct, the first sugar cane was introduced into Louisiana by the Jesuits in 1751, about thirty years after the founding of New Orleans. The canes grew to maturity, and were rather widely cultivated from then on; the stalks retailed in the markets of New Orleans as an article of luxury. Dubreuil, in 1759, built a sugar mill and attempted to make sugar, but this undertaking proved a complete failure.

The next step in the development of the industry is shrouded in uncertainty as to actual results, and only a few individuals continued to plant cane. However, two Spaniards, Mendez and Solis, continued its culture, the former making a sirup and the latter taffia (a kind of rum). In 1791 Mendez bought from Solis his distilling outfit, the land, and the cane, with the firm resolution to devote himself to sugar manufacture and to conquer all difficulties. For this purpose Mendez employed Morin, who had spent several years in Santo Domingo studying sugar cultivation and sugar manufacture. Apparently several barrels of sugar were made and experiments in refining were carried on, but there is no evidence to show that Mendez ever produced it in large and paying quantities.

The first crop of sugar large enough to influence the future of Louisiana and profitable enough to justify others to embark in the enterprise was made by Etienne De Bore in 1794, 1795, and 1796. In fact De Bore's first crop of sugar in 1795 sold for twelve thousand dollars—a large sum at the time. Like the majority of the planters of that time, De Bore had given his attention to the cultivation of indigo, and he had seen his hopes blasted and himself and family threatened with ruin. He therefore determined to undertake the growing of sugar cane and the manufacture of sugar.

To show the excitement prevailing in the community and the intense interest on the part of the planters, the following vivid description is given, by Gayare the historian, of the day on which the trial of sugar making was made:

"De Bore's attempt had not been without exciting the keenest interest; many had frequently visited him during the year to witness his preparations; gloomy predictions had been set afloat, and on the day when the grinding of the cane was to begin, a large number of the most respectable inhabitants had gathered in and about the sugar house to be present at the failure or success of the experiment. Would the syrup granulate? Would it be converted into sugar? The crowd waited with eager impatience for the moment when the man who watches the coction of the juice of the cane determines when it is ready to granulate. When that moment arrived, the stillness of death came among them, each one holding his breath and feeling that it was a matter of ruin or prosperity for them all. Suddenly the sugar

HISTORIC SUGAR KETTLE

This iron kettle, used by Etienne de Bore in 1795 for the first successful experiments in granulating sugar for commercial purposes in Louisiana, is preserved on the campus of the Louisiana State University.

[1] Presented before the Division of the History of Chemistry at the 103rd meeting of the A. C. S., Memphis, Tennessee, April 21, 1942.

maker cried out with exultation, 'It granulates,' and the crowd repeated, 'It granulates.' Each one of the bystanders pressed on to ascertain the fact on the evidence of his own senses and when it could no longer be doubted, they overwhelmed De Bore with congratulations and called him the savior of Louisiana."

The sugar maker who watched the cooking of the cane juice up to the moment of granulation was Antoine Morin, the same man associated with Mendez in his trials.

We thus see that De Bore, with Morin's help, was the first to show that cane sugar could be commercially produced from sugar cane grown in Louisiana, and is thus considered the founder of the sugar industry in this state.

Let us now proceed to show how the improvements introduced into the industry resulted in its tremendous development. While all the developments listed are not strictly chemical, they are included since the industry could not have expanded to the extent it did had any of these been lacking.

The first improvement was the introduction of the steam engine (1825), which replaced animal power for the turning of the mills. This also resulted in the placing of the rolls in a horizontal position and gave a better extraction of the juice and consequently of sugar. This was followed in 1830 by the introduction of the vacuum pan into Louisiana, which resulted in an improved grade of sugar. Coal replaced wood as fuel in 1840.

Rillieux in 1834 discovered multiple effect evaporation and, after ten years of experimental work, perfected and introduced in a Louisiana sugar house in 1844 the first multiple effect evaporator ever used. This was of tremendous importance since it not only resulted in a better grade of sugar but also in greater yields.

In rapid succession six roller mills (1847), centrifugals (1852), and bagasse burners (1853) were introduced into Louisiana practice. All these improvements resulted in a peak production of 264,000 tons of sugar in 1861.

The Civil War and the aftermath of economic and social changes almost caused the complete disappearance of the sugar industry and for a period of about twenty years little technical progress was made. Boiling back molasses to improve vacuum pan work and to obtain higher yields of sugar was first practiced in 1875. In the early 1880's shredders and crushers for preparing canes for the mills were introduced first into Louisiana and from here their use spread rapidly to the rest of the world.

At about this time, that is the late 1870's and the early 1880's, the planters began agitation for investigational work toward helping them solve their problems both in the field and in the sugar house. This attitude was brought about by the competition arising from the rapidly developing beet sugar industry. They also realized that their own investigations resulted in much duplication of effort, with no program set up to aid the industry as a whole. We have the beginning of cooperation among the planters, and their active support of research, which has continued uninterrupted to this day. We are now entering upon the golden age of chemistry in sugar industry, for we have the introduction of methods of chemical control that helped place our factories at a high level of efficiency. The United States Department of Agriculture sent to Magnolia, Louisiana, Harvey W. Wiley and G. L. Spencer. The former studied the chemical influences of soil, cane diseases, insect ravages, bacterial infection, and other plantation conditions upon the sugar-refining process; while the latter developed the diffusion process in cane work. This process, although never generally adopted, undoubtedly was instrumental in forcing mill designers to improve extractions and this finally led to the installation of the first nine-roller mills in the world at Cora plantation. It was here at Magnolia that the first filter press was used in a cane sugar factory in the Western Hemisphere.

It was in the course of this work that Dr. Spencer laid the foundation of his brilliant career as sugar technologist, exemplified so well in the numerous editions of his well-known "Handbook of Sugar Cane Manufacturers" and in his later capacity as supervisor of manufacturing on many sugar estates of Cuba. Working also with Dr. Wiley at this time were C. A. Crampton and Hubert Edson, who studied the chemical and technical control of the sugar house, and their work resulted in the production of over 200 pounds of sugar per ton of cane.

As a further means of improvement of the sugar industry, the Louisiana Scientific and Agricultural Society, an organization composed mainly of sugar planters, voted $60,000 for the financing of a sugar experiment station. The statement is made that this is the first research organization set up by any industry for the investigation of its problems, and if that is true it reflects the progressive and farsighted wisdom of the Louisiana planters of that day.

The first station was located at Kenner, Louisiana, a few miles northwest of New Orleans, where a small plantation of 100 acres, a sugar house, and several other buildings were purchased. The latter were converted into laboratories, which were well equipped with furnaces, ovens, balances, several polariscopes, and the usual supply of glassware, etc. W. C. Stubbs was brought in as the first director and together with two chemists and a sugar boiler started the Station on October 5, 1885. What the Station contemplated doing is set forth by Dr. Stubbs as follows:

1. "To test the question of growing more cane upon a given area and putting more sugar in the cane.
2. To study the political economy of the sugar cane.
3. To test the various methods, both scientifically and practically, of making sugar.
4. To disseminate information among the subscribers of the Station and to advance the sugar interests of Louisiana."

It is evident that he keenly grasped the needs of the planters and the main objectives of the Station. These statements of his, if generalized to cover all types of farming, still represent the goals of the federal and state experiment stations even today.

With the passage of the Hatch bill in 1887 in which provisions were made for the financing of state experiment stations in connection with the colleges of agriculture, the Board of Supervisors of the Louisiana State University on April 5, 1887, took over the supervision and maintenance of the Sugar Experiment Station, thereby relieving the sugar planters of further financial obligations. Up to this time the planters had donated $100,000 in cash and equipment. In this year the Station was moved to Audubon Park, on the outskirts of New Orleans, where it remained until 1925, when it was consolidated with the main station at the Baton Rouge campus.

The scope of the investigations carried on at the Station is indicated by the following topics taken from the titles of some of the *Bulletins:* The effect of sugar cane culture, fertilizers, varieties, etc., upon the yields and sucrose content of the cane, chemical control in the sugar house, clarification studies and decolorization, bacteriological studies of cane and cane products, etc. These were the subjects of exhaustive investigations and were reported in several series of bulletins. Personalities should not be neglected: W. C. Stubbs, J. L. Buson, Walter Maxwell, C. A. Browne, R. E. Blouin, W. E. Cross, M. A. Schneller, F. Zerban, H. P. Agee, and W. L. Owen, to mention just a few.

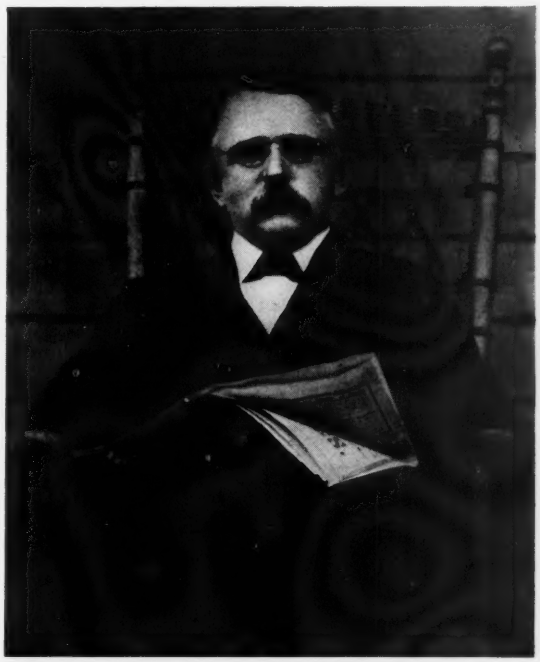
Through the work of the chemists of the United States Department of Agriculture and the Sugar Experiment Station it soon became evident to the planters that chemists could increase sugar recovery by preventing losses in the manufacturing process. However properly trained and qualified chemists were not available for taking charge of the sugar houses; so to overcome this deficiency the sugar planters in 1890 decided to establish in connection with the experiment station a school for the training of experts in sugar work and endowed it with private subscriptions. The school was placed under the direction of Dr. Stubbs and was opened in 1891 as the Audubon Sugar School. Dr. Stubbs in his biennial report of 1892 stated that the school was established because:

1. "Young men came to study sugar culture and manufacture and chemistry, and the number applying was in excess of the limited capacity of the station;
2. "Because of demand for sugar chemists young men left after very short and imperfect training. They would go with the prestige of having worked at the station and in event of failure to meet the expectation of the planters would invariably cast opprobrium upon the station;
3. "After training the young men in the laboratory and sugar house to a point where they could be useful to the station in the further prosecution of their work, they have invariably left the station at the opening of every season, leaving the station to prosecute its experiments in sugar manufacture with new and untried men."

The object of the school was stated as follows:

"It is designed by its regular course of two years to turn out experts capable from their training of directing any part of the sugar industry from the growing of the cane to its manufacture into the purest and whitest sugar, while its irregular course is planned to meet the requirements of the sugar maker and engineer who seek to add to their practical accomplishment and knowledge of the principles upon which their acts are based."

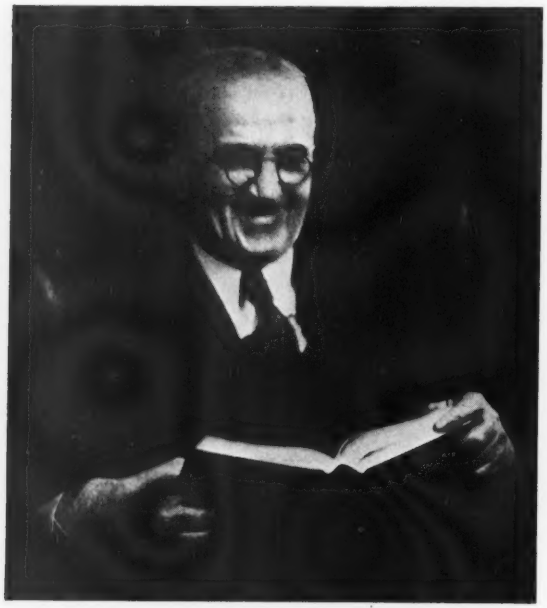
As first outlined, the Audubon Sugar School was intended to appeal mainly to graduates of technical courses and engineering. It soon became evident that the number of college graduates who appreciated the opportunities in the sugar industry was quite small, and the demand for training came mainly from men who had not received very much undergraduate training and from applicants from tropical countries whose preliminary studies had been of such a type as to make it impossible for them to take up successfully the advanced scientific work offered in the sugar school. In spite of this the school was successful from the outset, and in a few years more students were applying for admission than could well be accommodated. With limited funds, the increasing demands upon its staff along purely research lines, and the growing magnitude of its routine work, the station found it impossible to handle students also. In 1896 the school was, accordingly, incorporated with the Louisiana State University, preserving the name by which it had become known. The course was now set up as a full four-year course and resulted in the elimination of the irregular course and the exclusion of students who could not meet the college entrance requirements. In 1899 the course was further modified to a five-year course leading to the



DR. W. C. STUBBS

State Chemist of Alabama and Professor of Chemistry at Alabama Polytechnic College, 1869–85; Professor of Agriculture and Director of the Louisiana Experiment Station and State Chemist, 1885–1905.

B.S. degree. The first three years were given over to basic fundamental courses in chemistry, physics, mathematics, engineering, and biological sciences. In the fall terms of the fourth and fifth years the students were sent to the sugar house at Audubon Park to receive practical instructions in the operation of a sugar factory. At the end of the sugar season they returned to the University for the rest of the school year. The basic curriculum is still in operation today and stands as a testimony to the late Dr. Charles E. Coates, who was for many years the Dean of the Audubon Sugar School. This school is another contribution of the Louisiana sugar planters and the sugar industry to the chemical development of Louisiana, and is the first instance in America in which any industry established a school for the college training of men to put theory into practice.



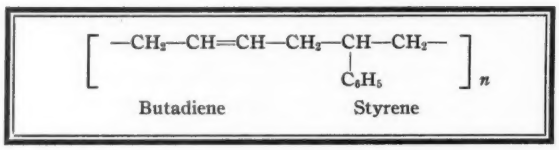
DR. CHARLES E. COATES

Professor of Chemistry at Louisiana State University, 1893–1937, and Dean of the Audubon Sugar School, Louisiana State University, 1907–37

The importance of these scientific developments which have been discussed is indicated by their effect upon sugar production in Louisiana. From a low production of 5000 tons of sugar in 1865 the amounts gradually increased until the early 1880's, and then rapidly grew to a maximum of 398,000 tons in 1904. From this maximum the amount decreased slowly but steadily until 1926 when the production totaled only 47,000 tons. Since then the production of sugar has increased rapidly until today Louisiana could produce regularly 600,000 tons per year if no acreage restrictions were imposed. This recovery from the disaster of 1924, 1925, and 1926 was accomplished through the introduction of disease-resistant canes and was brought about by the combined efforts of the plant pathologist and cane breeder. However, it is interesting to note the plant pathologist, in his study of plant diseases, is now calling upon the chemist for help so that if we are to maintain our present output of sugar it will require the chemist working in coöperation with the pathologist to make this possible.

We have traced the history of the sugar cane industry in Louisiana from its beginning in 1794 and have pointed out how the chemist has been responsible for its growth and development. The slow growth during its first 90 years, which resulted mainly from mechanical and chemical improvements in the methods of extraction and purification of sugar, was due to individual effort. No system of unified research had been devised. The planters, by financing the establishment of an experiment station and a sugar school and the coöperation of these with federal and state agencies, brought about a unified research program which resulted in improved cane and sugar yields, chemical control of sugar-house practice and decreased sugar-house losses. The value of the methods of chemical control resulting from this program is evidenced by the high state of development we have today.

FORMULA OF THE MONTH



THE MONOMER OF BUNA-S

Probably destined to be one of the most important of the synthetic rubber substitutes.

Color Nomenclature in Qualitative Analysis[1]

II. ISCC-NBS Color Names

L. P. BIEFELD and MARGARET GRIFFING *Purdue University, Lafayette, Indiana*

THE need for a systematic method of color designation in chemistry and the importance of color nomenclature in qualitative analysis was pointed out in the first paper of this series (*1*). A brief résumé of the Inter-Society Color Council-National Bureau of Standards method of color designation (*2*) and recommendation of the adoption of this method for determining color names of colored substances encountered in courses on qualitative analysis were given. This article includes a short description of the experimental procedure followed for obtaining the ISCC-NBS color names of these colored substances, a record of the names assigned, and a brief discussion of some of the results obtained.

Semimicro and macro technics were used for preparing the substances to be studied. Although procedures given in Middleton and Willard (*3*) and Curtman (*4*) were followed, some additional experiments were run according to directions given in other standard texts on qualitative analysis.

Color names were determined for freshly prepared moist precipitates; dry precipitates that were stable under normal atmospheric conditions and room temperatures; solid reagents; reagent solutions; test solutions; and solutions resulting from separations and identification tests. The materials were studied under conditions of student observation in the laboratory as well as under the more nearly ideal and specified standard conditions of illumination and viewing. The liquids were viewed by transmitted light.

PROCEDURE FOR COLOR DESIGNATION

Solids

Each precipitate was prepared by nearly complete precipitation of the test ion from a solution having a concentration of 10 mg. of ion per ml. The solid substance was filtered by suction, washed, and immediately introduced into a small aluminum holder whose depth was 2 mm. An optical cover glass was pressed down over the substance and holder with a rotary motion and clamped in place with rubber bands. The sample was placed under the center opening of a triple-apertured neutral gray comparison mask and identified with the nearest Munsell color chip (*5*), whose coördinates were recorded. The comparison chart and sample, illuminated by daylight falling from a north window at an angle of 45°, were viewed from almost directly above. A black canopy, hung above the sample and opposite the observer, eliminated reflections by the cover glass. The colors observed in this manner result totally from reflected light. The color name was obtained by plotting the Munsell coördinates on the boundary name charts published by Judd and Kelly (*2*). In order to check the reliability of the color readings and the reproducibility of the colors of the precipitates, the experiments were repeated.

In order to determine the effect of variation of temperature, hydrogen-ion concentration, and test-ion concentration, a series of preparations for each precipitate was carried out. Because the color name was not affected by the technic used, semimicro methods were used for the initial experiments because of their ease and speed. In case any of these variables were critical, larger quantities were prepared under extreme conditions and their color names determined. For these substances, the range of color names found is reported. All the precipitates were allowed to dry in the air and their color names were determined in the same manner. If they dried in a cake, they were ground to a powder before viewing.

The colored solids from which the test and reagent solutions were prepared were likewise studied. The solids existing as large particles were studied after grinding in a porcelain mortar. Before grinding, a single large piece was compared to the Munsell chip by holding the substance directly above the properly illuminated standard color charts. The color names obtained in this manner are less exact.

In order to check the validity of color names obtained from the individually prepared precipitates, solids formed in the course of an actual cation analysis were studied. For each of the cation groups, a solution was prepared in which the concentration of each ion was 2.5 mg. per ml. The regular separations and confirmatory tests were carried out, using both semimicro and macro technics. In each case of clear-cut separation, the color name of the solid so obtained was identical with that of the solid precipitated from a test solution.

Because the student must learn to correlate these color designations with the actual color by his observation in the laboratory, the color names were also determined for fresh precipitates viewed in centrifuge or test tubes. Using semimicro technic, the precipitates in the centrifuge tubes were compared to the standard Munsell charts using the method employed for determining color names of individual pieces of solid reagents. Colors observed in this manner result from the combined contribution of reflected and transmitted light. For this series of experiments, the charts and samples were illuminated from directly above by daylight fluorescent lamps and were observed at an angle of 45°. Even though these conditions of illumination were recommended as equivalent to the method of view-

[1] Presented before the Division of Chemical Education at the 103rd meeting of the A. C. S., Memphis, Tennessee, April 21, 1942.

ing previously described (*6*), a series of solids was studied under both conditions. The color names so obtained were identical.

Liquids

According to the ISCC-NBS method of color designation, the color names of liquids are determined by transmitted light only. The colored reagents and test solutions were prepared with concentrations varying from 0.1 *M* to 0.5 *M*. Liquid was introduced into a vial, made from a 50-ml. Nessler tube, to a depth of one cm. The vial was placed in a brass holder containing a round opening at the bottom equal in area to the aperture in a white shield. The apertures in the shield were surrounded by a black area. The sample was held 8 inches above the shield and the color resulting from the light reflected by the shield and transmitted by the liquid was identified with the proper Munsell chip and color name. Those identification and test solutions which could not be conveniently prepared within the range of concentrations mentioned were studied at the strength encountered in an actual analysis.

COLOR DESIGNATION OF PRECIPITATES

The precipitates studied are listed in Table 1. The representative common color names are in general those used by Middleton and Willard (*3*), Curtman (*4*), and Ware (*7*). It is interesting to compare these names with the systematic color names obtained for fresh moist precipitates, dried precipitates, and precipitates viewed in a glass tube.

As pointed out in the previous paper, certain substances may be designated by more than one color name because the color corresponds to a point on the border of two or more adjacent color name areas on the boundary name charts. This variation in color designation is indicated in the table by the use of "or" between two equally applicable color names. Actual variation in the color of a substance, due to variation in experimental conditions, is indicated by recording the color names designating the extreme limits of color obtained and connecting these names with the conjunction "to." However, the majority of precipitates studied did not exhibit sufficient color variation under different conditions to necessitate more than one color

TABLE 1
COLOR NAMES OF PRECIPITATES

*Name**	*Formula*	*Common Color Names*	*ISCC-NBS Color Names*		
			Fresh Precipitate	*Dry Precipitate*	*Fresh Precipitate Viewed in Glass Tube*
Aluminon lake	$Al(OH)_2$ Aluminon	Brilliant scarlet	Vivid red to deep purplish red	.....	Vivid red
Ammonium molybdophosphate	$(NH_4)_3[P(Mo_3O_{10})_4]$	Yellow	Strong yellow	Strong yellow or vivid yellow	Brilliant yellow or strong yellow
Ammonobasic aquobasic mercury (II) iodide	$H_2NHgOHgI$	Red-brown	Moderate brown or strong brown	.....	Brown
Diammonium sodium hexanitrocobaltate (III)	$(NH_4)_2Na[Co(NO_2)_6]$	Yellow	Dark orange or deep orange	Dark orange or deep orange	Deep yellowish orange
Antimony sulfide	Sb_4S_6	Orange-red, red-orange	Dark reddish orange or deep orange	.....	Deep orange or strong orange
Arsenic (III) sulfide	As_4S_6	Light yellow, canary-yellow, buff	Vivid yellow to strong greenish yellow	Moderate greenish yellow to strong yellow	Strong yellow
Barium chromate	$BaCrO_4$	Light yellow, pale yellow	Moderate greenish yellow	Moderate greenish yellow	Light yellow or moderate greenish yellow
Barium rhodizonate	BaC_6O_6	Red-brown	Dark reddish brown	.....	.....
Cadmium sulfide	CdS	Orange-yellow	Deep yellow to strong orange	Vivid yellow to deep orange	Strong yellow or vivid yellow
Calcium chromate	$CaCrO_4$	Deep yellow	Strong yellow	Strong greenish yellow	.....
Hydrated chromium (III) phosphate	$CrPO_4 \cdot xH_2O$	Green, dirty green	Weak purplish blue or medium bluish gray	.....	Medium bluish gray or dark bluish gray
Hydrated chromium (III) oxide	$Cr_2O_3 \cdot xH_2O$	Dirty green	Weak blue-green or dusky blue-green	.....	Medium greenish gray or weak blue-green
Cobalt (II) cyanide	$Co(CN)_2$	Russet brown, brown	Dark reddish gray or dusky red	.....	Weak red-purple
Cobalt (II) hydroxide	$Co(OH)_2$	Pink	Weak red or weak purplish red	.....	Weak red-purple
Cobalt (II) hydroxynitrate	$Co(OH)NO_3$	Blue	Dusky blue or weak purplish blue	.....	Moderate blue
Cobalt (II) alpha-nitroso-beta-naphtholate	$Co[C_{10}H_6(NO)O_3]$	Brown, crimson, brick red	Dark red or very dark red	Moderate reddish brown	Moderate reddish brown
Cobalt (II) hexacyanoferrate (II)	$Co_2[Fe(CN)_6]$	Green	Weak olive-green or moderate olive-green	.....	Dusky yellow-green or moderate olive-green
Cobalt (II) thiocyanatomercurate (II)	$Co[Hg(NCS)_4]$	Blue	Vivid purplish blue	Strong purplish blue	Vivid purplish blue
Copper (II) hexacyanoferrate (II)	$Cu_2[Fe(CN)_6]$	Dark reddish brown	Very dusky red or very dusky red-purple	Dusky red-purple or dusky purplish red	Very dusky red-purple
Copper (II) hydroxynitrate	$Cu(OH)(NO_3)$	Light bluish green, pale blue	Light blue or light greenish blue	.....	Light greenish blue
Copper (II) salicylaldoximate	$Cu(C_6H_6O_2N)_2$	Greenish yellow	Weak yellow-green	Weak yellow-green	Weak yellow-green
Copper (II) thiocyanatomercurate (II)	$Cu[Hg(NCS)_4]$	.....	Moderate yellowish green or dark greenish yellow	.....	Moderate yellow-green
Iron (III) hexacyanoferrate (II)	$Fe_4[Fe(CN)_6]_3$	Prussian blue	Black	Dusky purplish blue	Deep blue or dusky blue

* Compounds are named according to the rules given by the International Union of Chemistry for Reform of Inorganic Chemical Nomenclature, 1940. *J. Am. Chem. Soc.*, **63**, 889 (1941).

name. In this connection, it should be recalled that the coördinates of distinguishable colors may fall in the same name area and thus receive the same color designation.

If the composition of the precipitate seemed to change on drying, the color name of the dried substance was not determined. In many cases, only a slight difference in color was noted as a result of drying, so slight that the precipitate still had the same color designation. Often, the colors of those substances which did undergo distinguishable changes on drying exhibited increased chroma and value, and a shift in hue toward the blue end of the spectrum. For example, cadmium sulfide changed from deep to vivid yellow, and dimethylglyoxime from deep red to strong purplish red. This cannot be taken as a generalization, however, because there are too many exceptions. For example, potassium sodium hexanitrocobaltate (III) changed from dark orange to dark yellowish orange; and silver arsenate, from moderate reddish brown to weak reddish brown. Striking changes were shown by chromic phosphate and hydroxide; they were probably due to aging rather than drying. The phosphate was a medium bluish gray when freshly dried but, on standing in a glass vial, it became a light blue-green and continued to change with increasing chroma. The hydroxide changed from a weak blue-green to a moderate greenish blue and continued to change in the blue direction with continually increasing chroma.

Although the color names for the fresh precipitates viewed in centrifuge tubes were obtained by a rather crude comparison, they are reasonably accurate designations for the colors observed. In practically all cases the coördinates obtained for these colors fell within the same name area as those obtained under carefully controlled conditions of observation and illumination. There was a tendency for all the precipitates to exhibit decreased chroma and increased value. Notable examples are cadmium sulfide, ferric phosphate, and silver arsenite. The differences may possibly result from the presence of a small amount of the mother liquor sorbed by the solid.

The color of the cobalt (II) alpha-nitroso-beta-naphthol complex seemed to change from a dark red to

TABLE 1 (*Continued*)
COLOR NAMES OF PRECIPITATES

Name	*Formula*	*Common Color Names*	*ISCC-NBS Color Names*		
			Fresh Precipitate	*Dry Precipitate*	*Fresh Precipitate Viewed in Glass Tube*
Iron (II) hexacyanoferrate (III)	$Fe_3[Fe(CN_6)]_2$	Blue	Black	Dusky purplish blue	Deep blue or dusky blue
Iron (III) hydroxide	$Fe(OH)_3$	Reddish brown	Very dusky red or dusky reddish brown	.....	Moderate reddish brown
Iron (III) phosphate	$FePO_4$	.....	Weak yellow	Weak yellow	Yellowish white
Lead chromate	$PbCrO_4$	Orange-yellow	Strong yellow to moderate yellowish orange	Strong yellow or vivid yellow to moderate orange or strong orange	Strong yellow to moderate yellowish orange
Magnesium S. and O. lake	$Mg(OH)_2$·S&O	Sky-blue, red-violet	Deep purplish blue to moderate blue	.....	Moderate blue
Manganese (II) hexacyanoferrate (II)	$Mn_2[Fe(CN)_6]$	White to pink	Pale yellow-green or weak yellow-green	Pale yellow-green or weak yellow-green	White
Manganese (II) sulfide	MnS	Flesh, salmon-pink	Pinkish gray or weak orange-pink	.....	Pinkish white or pale orange-pink
Mercury (II) iodide	HgI_2	Orange-red, scarlet	Strong red or strong reddish orange	Strong red or strong reddish orange	Moderate reddish orange or strong reddish orange
Nickel (II) dimethylglyoximate	$Ni[(CH_3)C_2NOHNO]_2$	Pink, brilliant scarlet	Deep red	Strong purplish red	Strong red or deep red
Nickel (II) cyanide	$Ni(CN)_2$	Very light green	Pale blue or light blue	Pale blue or light greenish blue	Very pale blue
Nickel (II) hexacyanoferrate (II)	$Ni_2[Fe(CN)_6]$	Light green	Light green or light bluish green	Light green	Very light green or light green
Nickel (II) hydroxynitrate	$Ni(OH)NO_3$	Light green	Light green	Very pale green or very light green	Light bluish green
Nickel (II) hydroxide	$Ni(OH)_2$	Light green	Light green or moderate green	Light green or very light green	Light green
Potassium hexanitrocobaltate (III)	$K_3[Co(NO_2)_6]$	Orange-yellow	Strong yellow	Strong yellow	Strong yellow
Dipotassium sodium hexanitrocobaltate (III)	$K_2Na[Co(NO_2)_6]$	Orange-yellow	Dark orange or deep orange	Dark yellowish orange or deep yellowish orange	Dark yellowish orange
Silver oxide	Ag_2O	Brown, black	Weak brown or moderate olive-brown	.....	Weak brown
Silver arsenate	Ag_3AsO_4	Reddish brown, chocolate-brown	Moderate reddish brown	Weak reddish brown	Pale reddish brown
Silver arsenite	Ag_3AsO_3	Light yellow	Moderate yellow or dark yellow	.....	Moderate yellow
Silver chromate	Ag_2CrO_4	Red, crimson	Moderate reddish brown or dark reddish brown	Dusky red	Dark red or moderate reddish brown
Silver hexacyanoferrate (III)	$Ag_3[Fe(CN)_6]$	Orange-red, brown	Dark reddish orange	.....	Dark orange or deep orange
Silver iodide	AgI	Light yellow	Pale yellow-green or light yellow-green	.....	Weak greenish yellow
Silver phosphate	Ag_3PO_4	Yellow	Moderate greenish yellow	.....	Light greenish yellow or moderate greenish yellow
Strontium chromate	$SrCrO_4$	Deep yellow	Moderate greenish yellow	Moderate greenish yellow	.....
Tin (IV) sulfide	SnS_2	Light yellowish brown, buff	Dark yellow or moderate yellow	.....	Moderate yellow
Tin (II) sulfide	SnS	Yellowish brown	Dusky brown	.....	Dusky brown

a moderate reddish brown—similar to the change on drying. However, since the alpha-nitroso-beta-naphthol reagent is brown this difference is probably attributable to the excess necessary for precipitation. The color names of strontium chromate and calcium chromate were not determined using semimicro technic because each is precipitated only from hot concentrated solutions.

The colors of both the aluminon and S. and O. lakes were affected by the changes in concentration of the metal ion. Using equal volumes of metal-ion test solutions and reagents, the aluminon lake was designated as vivid red and the S. and O. lake as deep purplish blue; but, if the volume ratio of reagent to test solution was 1 to 10, the aluminon lake became deep purplish red and the magnesium lake, moderate blue. A study of other relative concentrations revealed that the above color names designated the extreme colors which might be encountered in the qualitative analysis laboratory.

The colors of the Group II sulfides have long been of interest to chemists because of their great variety. Every preparation of antimony sulfide resulted in a compound whose color coördinates were on the border between dark reddish orange and deep orange name areas. However, arsenic (III) sulfide exhibited a variation in color from vivid yellow to strong greenish yellow on changing the condition of precipitation from cold 0.3 *M* hydrochloric acid to hot 12 *M* hydrochloric acid. The concentration of arsenic (III) ion was not critical. Mellor (*8*) states that the arsenic (III) sulfide is obtained by treating an acidic solution with hydrogen sulfide gas; if sufficient gas is added, some sulfur is precipitated. It is possible that this sulfur may account for the slight variation noted. Likewise, according to Mellor (*9*) mercury forms two red sulfides in addition to the black. These are prepared by heating the black sulfide in the presence of excess sodium sulfide. These modifications are very seldom encountered in qualitative analysis. Upon treating mercury (II) ion in 12 *M* hydrochloric acid with hydrogen sulfide gas a weak greenish yellow compound was precipitated. According to Middleton and Willard (*10*) this compound is a salt with the composition $2HgS{\cdot}HgX_2$. It is likewise stated that by continued treatment with hydrogen sulfide, various complexes with colors varying through brown to black may be prepared. However, only the weak greenish yellow and black colors were obtained. The colors of tin (IV) sulfide seemed unaffected by changes of concentration, temperature, and hydrogen-ion concentration within the range in which it is precipitated. Although only a sulfide which is dark or moderate yellow has been obtained, Middleton and Willard (*11*) report a buff-colored precipitate which is a mixture of SnS_2 and white $SnO_2{\cdot}H_2O$. Mellor (*12*) likewise states that such a mixture and some sulfur are obtained upon first precipitating the tin (IV) ion complex with hydrogen sulfide in an acidic solution. Tin (II) sulfide, obtained by treating a solution of Tin (II) ion in 0.3 *M* hydrochloric acid with hydrogen sulfide, was dusky brown. Although Mellor (*13*) reports the formation of a variety of sulfides with colors varying from orange-red to black, no other color was obtained by a variation of conditions. The colored crystals are thought to be salts such as Sn(SH)Cl. Further attempts will be made to obtain these and determine their colors.

Perhaps the most interesting of the sulfides is cadmium sulfide. In early experiments, it was noted that the first precipitate formed was a light yellow and that the color of the compound changed toward red as precipitation continued. Neither the metal-ion concentration nor the hydrogen-ion concentration was critical; the temperature seemed to affect only the speed with which completeness of precipitation was attained. From this series of experiments, it was concluded that completeness of precipitation was the important factor. A range of color names was obtained from deep or vivid yellow to a strong orange. Mellor (*14*) discusses the possible reason for this wide variation in color, and mentions two as possible: compound formation or particle size dependent primarily upon the rate of precipitation. Mellor discounts the evidence for compound formation and expresses the belief that it is merely a matter of particle size. The problem is being investigated in more detail.

TABLE 2
COLOR NAMES OF SOLID REAGENTS AND STOCK CHEMICALS

	ISCC-NBS Color Names	
Formula	*Fine Powder*	*Aggregates*
CdS	Moderate yellowish orange	
$CrCl_3{\cdot}6H_2O$	Very dusky green	Very dusky green
$Co(NO_3)_2{\cdot}6H_2O$	Light red or strong pink	Dark reddish orange
$Cu(NO_3)_2{\cdot}3H_2O$	Strong purplish blue	Strong or vivid blue
$FeCl_3{\cdot}6H_2O$	Strong yellow or vivid yellow	Dark yellowish orange or deep yellowish orange
$Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$	White	Very pale blue-green or bluish white
$MnCl_2{\cdot}4H_2O$	Pinkish white	Pale pink
MoO_3	Yellowish white or pale yellow-green	
$Ni(NO_3)_2{\cdot}6H_2O$	Light green	Brilliant green
$2MoO_3{\cdot}2H_3PO_4{\cdot}x(H_2O)$	Strong yellow or vivid yellow	
K_2CrO_4	Moderate greenish yellow	
$K_2Cr_2O_7$	Strong orange	
$K_4Fe(CN)_6$	White	Moderate greenish yellow
$K_3Fe(CN)_6{\cdot}3H_2O$	Moderate yellowish orange	Moderate reddish brown or strong reddish brown
$KMnO_4$	Very dusky purplish red	
$NaBiO_3$	Moderate yellow	
$Na_2Fe(CN)_5NO{\cdot}2H_2O$	Weak orange	Dusky red or very dusky red

Lead chromate was prepared having colors ranging from strong yellow to moderate yellowish orange. The concentrations of the lead, chromate, and hydrogen ions were not critical. However, the temperature seemed to be the determining factor. The yellow compound was obtained from a cold solution and the orange compound from a hot solution. This is in agreement with Mellor (*15*) who attributes the difference to the particle size and to the extent of hydration. He states that the yellow variety is more hydrated than the orange.

TABLE 3
COLOR NAMES OF FRESHLY PREPARED SOLUTIONS

Solute	*0.5 M*	*0.4 M*	*0.3 M*	*0.2 M*	*0.1 M*
$Co(NO_3)_2 \cdot 6H_2O$	Strong purplish red	Light purplish red or strong purplish red	Light purplish red or strong purplish red	Light purplish red	Moderate pink
$CrCl_3 \cdot 6H_2O$	Dark green or very dark green	Dark green or very dark green	Dark green	Strong green	Moderate bluish green
K_2CrO_4	Strong greenish yellow	Strong greenish yellow or moderate greenish yellow	Strong greenish yellow	Strong yellow	Strong yellow
$Cu(NO_3)_2 \cdot 3H_2O$ + excess NH_3	Vivid bluish purple	Vivid bluish purple	Vivid bluish purple	Vivid bluish purple	Vivid purplish blue
$Cu(NO_3)_2 \cdot 3H_2O$	Light blue-green	Light blue-green	Light blue-green	Very pale blue	Faint bluish color
$K_2Cr_2O_7$		Strong orange	Strong orange	Strong orange	Strong orange
$FeCl_3 \cdot 6H_2O$	Strong yellowish orange	Moderate yellowish orange	Moderate yellowish orange	Strong yellow	Strong yellow or moderate yellow
$Ni(NO_3)_2 \cdot 6H_2O$	Light green	Light green	Very light green	Pale yellowish green	Very pale green
$K_4[Fe(CN)_6]$	Light yellow-green	Light yellow-green or pale yellow-green	Light yellow-green or pale yellow-green	Pale yellow-green	Pale yellow-green
$K_3[Fe(CN)_6]$	Strong greenish yellow	Strong greenish yellow	Strong yellow-green	Brilliant yellow-green	Brilliant yellow-green

When viewed by reflected light only the fresh precipitates of both iron (II) cyanoferrate (III) and iron (III) cyanoferrate (II) appeared black. Upon drying, as is generally true, the apparent chroma increased and the color became dusky purplish blue. Viewed by partially transmitted light in a centrifuge tube, the color of the substance was designated as deep or dusky blue.

Ammonium hexanitrocobaltate (III) was not affected by variation in conditions of precipitation, even in an excess of each reagent. However, the sodium hexanitrocobaltate (III) in excess was effective in determining the color of the potassium salt. In the presence of a large excess of potassium ion a strong yellow compound was precipitated and in the presence of a large excess of the sodium hexanitrocobaltate (III) a dark orange precipitate resulted. According to Cunningham and Perkins (*16*), an excess of potassium ion gives potassium hexanitrocobaltate (III), $K_3Co(NO_2)_6$, and an excess of the reagent gives dipotassium sodium hexanitrocobaltate (III), $K_2NaCo(NO_2)_6$. If neither is in excess, a mixture of the two compounds results.

COLOR DESIGNATION OF SOLID REAGENTS

As shown in Table 2, the grinding of large hydrated crystals tends to decrease their chroma and increase their value. The hue is definitely changed in many cases but no generalization can be made. Only the hue names of the large pieces are significant since the reliability of the adjective is critically dependent upon particle size. For example, a single crystal of iron (II) ammonium sulfate seemed colorless, but a group of these crystals was colored a very pale blue-green.

COLOR DESIGNATION OF LIQUIDS

A study of the effect of variation in concentration on colors of freshly prepared solutions revealed that the hue changes. This is shown in Table 3. There seems to be a definite tendency for the change to be toward the blue. As would be expected, the value is increased and chroma is decreased with decreasing concentration. Solutions of chromium (III) chloride were very unstable. The differences indicated were observed after standing overnight. It will be noted that through the concentration range shown, the dichromate ion exhibited no change. However, on dilution to 0.05 *M*, it became a strong yellowish orange. It must be pointed out that the entire color name may be used only when the solution is viewed by transmitted light and through a depth of one cm. Just the hue name should be used if the concentration is roughly known.

TABLE 4
COLOR NAMES OF SOLUTIONS FRESHLY PREPARED ACCORDING TO MIDDLETON AND WILLARD (*3*)

Name	*Color Name*
Aluminon reagent	Deep reddish orange or strong reddish orange
Ammonia + Nessler's reagent	
0.5 mg./ml.	Dark yellowish orange
0.25 mg./ml.	Weak yellowish orange or moderate yellowish orange
0.05 mg./ml.	Moderate yellow
0.025 mg./ml.	Moderate yellow
0.0125 mg./ml.	Moderate yellow
Pentaaquoamminechromium (III) ion	Moderate red-purple
Hexamminecobalt (III) ion (very unstable)	Dark orange
Hexacyanocobaltate (II) (unstable)	Light yellowish green
Hexacyanocobaltate (III) (unstable)	Dark yellowish orange
Iron (III) hexacyanoferrate (III) (very dilute before light was transmitted)	Strong yellowish brown
Hexathiocyanatoferrate (III) (extremely dilute)	Vivid red
Hexaacetatoferrate (III)	Moderate orange
Trioxalatoferrate (III)	Moderate yellowish green or strong yellowish green
Perchromic anhydride	Vivid purplish blue
Permanganate ion	
0.02 *M*	Deep purple
0.01 *M*	Deep purple
0.005 *M*	Strong reddish purple or deep reddish purple
0.002 *M*	Vivid red-purple
S and O reagent	Strong reddish purple or deep reddish purple
Sodium hexanitrocobaltate (III) reagent	Strong reddish orange or deep reddish orange

In Table 4 are listed miscellaneous solutions whose color names are applicable if prepared according to Middleton and Willard (*3*).

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(12) MELLOR, *loc. cit.*, Vol. III, p. 598.
(13) MELLOR, *loc. cit.*, Vol. VII, p. 465.
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FOURTH SUMMER CONFERENCE OF THE NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

UNIVERSITY OF NEW HAMPSHIRE, DURHAM, NEW HAMPSHIRE

August 11–14, 1942

PROGRAM

Tuesday Evening, August 11

7:30—Motion Picture Program.
8:15—OFFICE OF THE PRESIDENT, *University of New Hampshire.* Welcome.
8:30—ARTHUR R. DAVIS, *Massachusetts Institute of Technology.* Fire and the Control of Fire.

Wednesday Morning, August 12

9:00—FRANK G. LANKFORD, *University of Virginia.* Experimental Evidence on the Relative Value of Individual Laboratory Work and the Demonstration Method in Teaching Science.
10:00—GORDON P. PERCIVAL, *University of New Hampshire.* Modern Methods of Soil Testing.
11:00—CARLE R. HAYWARD, *Massachusetts Institute of Technology.* Chemistry and Physics Applied to Extracting Metals from Ores.

Wednesday Afternoon, August 12

2:00—LEALLYN B. CLAPP, *Brown University.* Sulfamic Acid and Its Uses.
3:00—Symposium—Atomic Structure. JOHN E. CAVELTI, Chairman, *Allegheny College.*
4:00—Round Table Discussion. Laboratory Versus Demonstration.

Wednesday Evening, August 12

7:30—Motion Picture Program.
8:15—RALPH W. GERARD, *University of Chicago.* Science Education and the Contemporary World.

Thursday Morning, August 13

9:00—CHARLES H. STONE, *English High School,* Boston, Massachusetts (Retired). Guide Posts to Successful Teaching. Oxidation and Reduction.
10:00—ALBERT F. DAGGETT, *University of New Hampshire.* Spectrochemical Analysis.
11:00—MAJOR WILLIAM O. BROOKS, C.W.S., *United States Army.* What the Chemical Warfare Service Is Doing.

Thursday Afternoon, August 13

2:00—FRANK SCHNEIDER, *Queens College.* Microchemical Demonstrations as a Teaching Tool.
3:00—Symposium—Atomic Structure.
4:30—Round Table Discussions. (I) The Fused Course; (II) The Teaching of Elementary Organic Chemistry.

Thursday Evening, August 13

7:30—Motion Picture Program.
8:15—ROBLEY D. EVANS, *Massachusetts Institute of Technology.* Atom Smashing and the Structure of Atomic Nuclei.

Friday Morning, August 14

9:00—ERNEST G. RITZMAN, *University of New Hampshire.* Calories in Wartime.
10:00—KATHARINE B. BLODGETT, *General Electric Company.* Interference Colors Reflected by Thin Films.
11:00—C. HAWLEY CARTWRIGHT, *Corning Glass Works.* Invisible Glass.

Friday Afternoon, August 14

2:00—REVEREND JOSEPH J. SULLIVAN, S.J., *Holy Cross College.* Glass Blowing.
3:00—Symposium—Atomic Structure.
4:30—Round Table Discussion. The Effect of the War on Chemistry.

Friday Evening, August 14

7:30—Motion Picture Program.
8:15—ALEXANDER SILVERMAN, *University of Pittsburgh.* Glass Today and Tomorrow.

TRANSPORTATION

Durham is on the Western Division (via Dover) of the Boston and Maine Railroad. Frequent service is available all day. Reasonable taxi service is available from Dover for those trains which do not stop at Durham. The Durham railroad station is a two-minute walk from the registration desk of the dormitory. Bus service from Boston is also available. Telephone connections are available at James Hall (registration) and Congreve North (dormitory).

EXPENSES

Registration Fees

All teachers of chemistry in attendance at the conference are required to register.

Members, if paid before August 1, 1942, $2.00; if paid after August 1, 1942, $3.00.

Non-members, $5.00.

(At the option of the registrant, three dollars of this fee may be used in payment of dues for membership for one year in the Association.)

Non-professional

Guests of members or registrants, per family, $1.00.

Rates

Room, $1.00 per night; $3.00 for 4 nights.

Meals, about $1.25 per day.

The committee will attempt to make any special rooming arrangements that are desired, if they are notified in advance of the conference. All inquiries concerning the Fourth Summer Conference should be addressed to the Conference Chairman, Millard W. Bosworth, Saxtons River, Vermont.

SUMMER CHANGE OF ADDRESS

UNTIL September 1, all correspondence for the Editorial Office of the JOURNAL should be addressed to: JOURNAL OF CHEMICAL EDUCATION, WOODS HOLE, MASSACHUSETTS.

Methyl Methacrylate as Imbedding Agent

H. F. HALENZ and L. W. BOTIMER

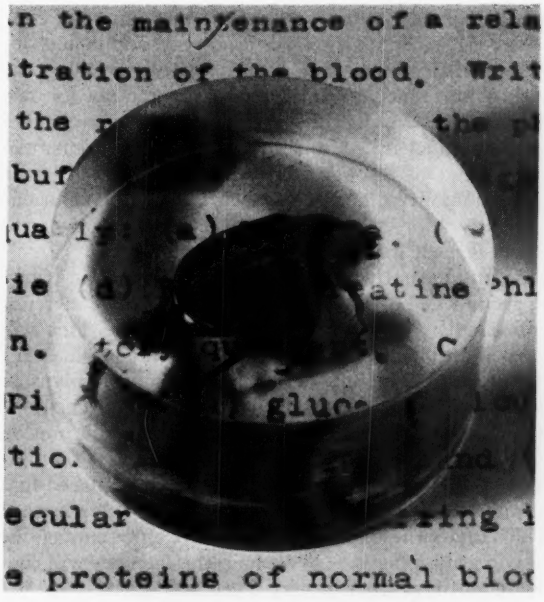
Emmanuel Missionary College,
Berrien Springs, Michigan

METHYL methacrylate monomer gives, upon polymerization, a colorless, highly transparent solid which in recent years has found many industrial applications. Because of its optical properties and relative ease of handling, it may be used as a medium for the imbedding of many types of objects for purposes of preservation or display, etc.

So far as the writer is aware, work of this nature, as yet unpublished, was first done some years ago by C. E. Sando of the Bureau of Chemistry and Soils. Hibben (*1*) at about that time reported on imbedding of some biological specimens. Inquiry among teachers of chemistry reveals a definite interest in this use of methyl methacrylate, though none of those asked had attempted to carry out the process.

The starting material is the monomer, obtainable from the E. I. du Pont de Nemours and Company (*2*). Pertinent information on this and other methacrylate resins will be found in the recent literature (*3*, *4*, *5*).

The monomer is a clear, colorless liquid of characteristic odor. Polymerization of the commercial product



is prevented by the addition of a trace of inhibitor. The latter may be removed by vacuum distillation through a short packed column (boiling point 100°C. at 760 mm., 61°C. at 200 mm.). A simpler method is to wash out the inhibitor by shaking equal quantities of a two per cent aqueous sodium hydroxide solution and monomer in a separatory funnel. The heavier alkaline solution is discarded. The washing process should be repeated until the alkali layer remains colorless; the monomer is then washed twice with distilled water. Any water remaining is removed by the use of calcium chloride or anhydrous sodium sulfate. The uninhibited monomer may be kept in a refrigerator for several days.

A small amount of the monomer is now carefully refluxed until it becomes thick enough to retain bubbles. This will take but a few minutes. Only sufficient material should be prepared to use within a day. The monomer nearest the container walls thickens more quickly; upon shaking it redissolves in the less viscous portion of the liquid. When it has cooled there is added about 0.1 per cent by weight of benzoyl peroxide. The latter speeds up the polymerization very appreciably. The amount of benzoyl peroxide to be used is somewhat critical; solidification takes place rather slowly if less than 0.05 per cent by weight is used; a larger amount tends to increase bubble formation; even frothing may occur.

The partially polymerized material is now transferred to a mold. An ordinary wide-mouthed bottle is quite satisfactory. It is placed in an oven at 45° to 50°C. and will become quite hard in from one to two days. A higher temperature increases the reaction rate, but also the extent of bubble formation. During polymerization the container must be tightly stoppered, since the monomer is highly volatile. A foil-covered stopper is advised. When a layer of the material, of suitable thickness, has solidified, the specimen to be imbedded is placed on it and partly polymerized monomer is poured around it. The heating process is then continued. When the polymer has become solid the temperature

may be raised to 80° or 90°C. in order to make certain that polymerization is complete. The material will become perfectly hard at the lower temperature also if sufficient time is allowed. The temperature to be used will depend on the nature of the specimen which is imbedded.

In order to prevent the formation of bubbles and the distortion of any specimens that may not be perfectly rigid, it is advisable to add the prepared monomer in two or three installments. The various layers will blend smoothly; no line of demarcation is ordinarily apparent. Casts prepared in this fashion show no evidence of strain under polarized light.

The material may be colored by use of certain dyes. Many of the more common dyes will not dissolve in methyl methacrylate, but among those which were found useful are Chrysarobin, Sudan III, and Indianthrene Brilliant Violet, which give light brown, red, and purple colors, respectively.

An idea of the appearance of objects imbedded by the above method may be obtained from the photographs.

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MERCURY VAPOR MADE VISIBLE

H. C. FROELICH

Lamp Development Laboratory, General Electric Company, Cleveland, Ohio

MERCURY vapor in the laboratory is a hazardous substance shunned by many and quite neglected by many more, particularly students. Lack of concern is due chiefly to the fact that mercury vapor does not attract sensory attention or sound a warning because at room temperature it can neither be seen nor smelled. Its vapor pressure is so low—of the order of one micron (10^{-4} cm.) at ordinary temperatures—that spilled droplets do not seem to become smaller in size if left in the open for many weeks, or even months. The following experiment will give a rather striking demonstration that mercury *does* evaporate at room temperature at a continuous and fairly rapid rate. It should prove valuable to impress students with the necessity of treating with greater respect stray drops of mercury of all sizes that can be found at random in most laboratories.

A pool of mercury about the size of a dime is placed on a small dish or in a plastic or wooden cup as shown in Figure 1. The mercury is covered completely with a fluorescent powder and the surface leveled with a spatula. The powder must be excitable by the short ultra-violet mercury radiation of 2537 Angströms. Any

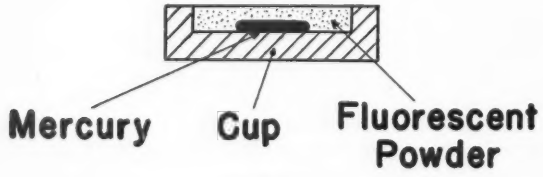


FIGURE 1

fluorescent silicate or tungstate will do; for example, zinc or zinc-beryllium silicate, calcium or magnesium tungstate, etc. These powders are readily available on the market at small cost.

A good source of 2537 A. radiation for the purpose is a 4- or 8-watt germicidal lamp mounted in a standard fluorescent fixture with suitable auxiliaries. These low-pressure mercury lamps emit the greater part of their energy in the 2537 A. region. Care must be taken that the lamp be shielded in order that no harmful radiation may reach the unprotected eyes of the observer. Germicidal lamps, in contrast to ordinary fluorescent lamps, are made of a special glass which is transparent to the short ultra-violet rays generated within.

When the powder sample is brought close to the light source, dark clouds or shadows will be seen passing over it. These clouds move more rapidly if light air currents are created, such as by blowing gently over the sample. Mercury evaporates at a rather constant rate through the thin covering layer of powder. Directly over the powder the vapor absorbs the resonance radiation 2537 A. strongly and this in turn prevents the phosphor underneath from becoming excited, thus creating the dark cloud effect. The mercury vapor casts its own shadow in 2537 A. light. Air currents carry the cloud of mercury vapor away from the sample, leaving momentarily clean air through which the ultra-violet rays can travel unhindered and excite the powder until sufficient mercury vapor has again collected over the powder to start the cycle anew. This takes but a second.

As an alternative, powder and a little mercury may be ground together in a mortar to disperse the mercury into smaller drops of larger total surface. This will intensify the effect. Greatest dispersion of mercury can be obtained as follows. About 5 g. of phosphor are placed in a 10-cc. glass bulb with a stem attached. A small drop of mercury, not more than 1.5 to 2 mm. in diameter, is introduced into the bulb, which is then exhausted and sealed off. Bulb and stem are placed in a furnace at 450° to 500°C. to vaporize all mercury, which under these conditions will have a pressure of one to two atmospheres. On cooling, the mercury will condense on the powder in very fine subdivision.

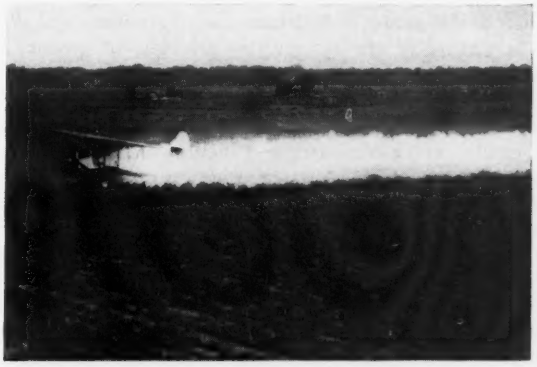
The Search for New Insecticides[1]

H. L. HALLER

Division of Insecticide Investigations, Bureau of Entomology and Plant Quarantine, United States Department of Agriculture, Washington, D. C.

THE use of chemicals to combat destructive insects has been practiced for many years. Sulfur and arsenic are probably the oldest insecticides of which there are records (*1*). The former was mentioned by Homer about 1000 B.C., and the Chinese used arsenic sulfides as early as 900 A.D. to control insects on plants. A variety of other materials, such as hot water, brine, lye, whitewash, soap suds, vinegar, petroleum, turpentine, fish oil, and decoctions of aloes, pepper, soot, tobacco, and wormwood, have also been used as insecticidal agents for a long time. Marco Polo in his writings at the end of the thirteenth century mentions mineral oil for anointing camels afflicted with the mange. Arsenic and honey mixture was recommended more than 250 years ago for the control of ants. Tobacco dust was advocated in France for use against plant lice in 1690. Pyrethrum, or common insect powder, and derris also have been used for more than one hundred years. Peter Kalm, a Swedish scientist who visited this country in 1748–49, in his book "Travels in North America" (*2*), refers to the insect pests encountered by him and the materials or remedies used for their destruction. Among the materials mentioned are a decoction of white mullein, *Verbascum thapsus*, for the control of worms infesting the wounds of cattle (*2a*); the burning of sulfur for the control of bedbugs (*2b*); an extract of hellebore root, *Veratrum album*, to be used when children "are plagued with vermin" (*2c*); and shavings and chips of red cedar distributed in clothing to protect it against being worm eaten (*2d*).

Little progress, however, in the systematic control of insects was made in this country until about 1867, when Paris green, which was available because of its use as a paint pigment, was tested against the Colorado potato beetle. The results were so satisfactory that for many years it was the standard treatment for the control of this pest on potatoes and it is still used to the extent of about two million pounds annually for the control of insects on garden crops. In 1892 lead arsenate was introduced as an insecticide for the control of the gypsy moth, against which it is particularly effective. In a short time lead arsenate replaced Paris green as an insecticide for plants and today is still used more extensively than any other arsenical or insecticide for the control of insect pests. In 1920 about 30 million pounds of lead arsenate were used and since that time there has been a steady increase to about 60 million pounds in 1940. Other arsenicals used in large amounts are calcium arsenate and white arsenic (arsenious oxide). The former, developed about 1915 for the control of the boll weevil, is used in approximately two-thirds the quantities of lead arsenate. White arsenic,



Courtesy of U. S. Department of Agriculture, Bureau of Entomology and Plant Quarantine

AIRPLANE DUSTING COTTON FOR BOLL WEEVIL CONTROL

owing to its caustic qualities, cannot be applied to foliage, but it is used in large quantities in poisoned baits for killing grasshoppers and in the form of an alkaline solution for the dipping of cattle to eradicate ticks. About 4 or 5 million pounds are used annually for these purposes. Besides lead and arsenic, insecticidal preparations may contain antimony, fluorine, thallium, selenium, and mercury. Copper and sulfur are usually constituents of fungicides.

Lead, arsenic, fluorine, etc., are toxic elements, and the use of more than 100 million pounds annually of arsenical preparations, much of which is applied to fruit and vegetables, is of considerable concern to health authorities and the general public. The action of public health authorities in insisting upon limits of tolerance of lead, arsenic, and fluorine has stimulated search for substitutes. Since other inorganic compounds would also leave spray residues that might be health hazards, the trend in the development of new insecticides has been toward organic compounds.

Organic insecticides may be divided into three broad classes: (*a*) those of animal origin; (*b*) those of plant origin; and (*c*) those prepared synthetically. The first class includes fish oils, whale oils, fats, glue, gelatin, and petroleum oils, which may be derived from either plant or animal life of former geological periods. Owing to their comparatively low toxicity, materials of animal origin do not appear to be promising sources of insecticides.

Of the several hundred plants (*3*) tested for insecticidal properties only a few have shown enough promise to

[1] Adapted from the address of the retiring president, Chemical Society of Washington, January 8, 1942.

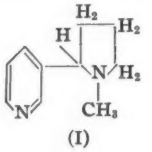
be of commercial value. Tobacco, *Anabasis aphylla*, pyrethrum, derris, and related plants are the more important. Quassia and hellebore are of lesser value. Tobacco owes its insecticidal properties primarily to nicotine, but recently a variety of tobacco in which nornicotine (*4*) predominates has been receiving attention for possible commercial utilization as an insecticide. The toxicity of pyrethrum is due to the pyrethrins, of which there are two. Rotenone, deguelin, and toxicarol are the principal constituents of derris and related plants. Alkaloids are responsible for the insecticidal action of hellebore and of *Anabasis aphylla*. The nature of the insecticidal principle of quassia is unknown.

Nicotine, anabasine, the alkaloids of hellebore, pyrethrins, and rotenone possess complicated structural formulas, and a comparison of them reveals no common grouping to which insecticidal action might be attributed. Nicotine and anabasine have been synthesized in the laboratory, but the prospects are not bright for their commercial manufacture. The pyrethrins and rotenone possess such complicated structures that there is little hope for their synthesis in the laboratory, much less on a commercial scale. The structures of the hellebore alkaloids have not yet been fully elucidated. Nevertheless, because of their outstanding value as insecticides the chemist turns to these plant products for guidance in the preparation of simpler compounds that might be useful in the control of insect pests.

In the paragraphs to follow the chemistry of these natural insecticides and some of the more closely related compounds that have been prepared and tested for insecticidal properties are briefly presented.

NICOTINE AND RELATED COMPOUNDS

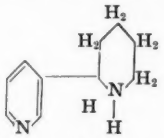
The source of nicotine is the tobacco plant, which belongs to the solanaceous genus *Nicotiana* and of which there are about 100 species. Only two, *Nicotiana tabacum* and *N. rustica*, however, are of importance for the commercial production of nicotine. Pure nicotine is a high-boiling, water-soluble liquid. It has the em-



(I)

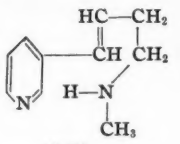
pirical formula $C_{10}H_{14}N_2$. Its structure (I) was established by Pinner (*5*) in 1893 as a ditertiary base, β-pyridyl-α-N-methyl pyrrolidine. This was confirmed through synthesis by Pictet and Rotschy (*6*). Recently newer syntheses have been devised by Späth and Bretschneider (*7*) and by Craig (*8*). Nicotine possesses an asymmetric carbon atom and, like all such compounds that occur naturally, is optically active. The natural product is levo-rotatory, but the dextro-rotatory form (*9*) has also been prepared. A comparison of their insecticidal properties (*9*) shows the naturally occurring product to be the more toxic, an indication that spatial configuration in these compounds plays an important part in their insecticidal action.

In an effort to determine whether the toxicity of nicotine is specific for the whole molecule or whether this effect is due to some special grouping of its component parts, a number of closely related compounds have been synthesized and tested. Among them are dipyridyls (*10*, *11*), dipiperidyls (*12*, *13*), pyridyl piperidines (*13*, *14*), and pyridyl pyrrolidines (*15*, *16*), as well as simpler derivatives of pyridine (*17*) and pyrrolidine (*19*). With the exception of one compound, 3-pyridyl-2′-piperidine [neonicotine (II)] (*14*), which is of the same order of toxicity as nicotine, all of the synthetic derivatives were distinctly inferior as insecticides.



(II)

Neonicotine, obtained as one of the reaction products of sodium and pyridine, is of interest in that shortly after its synthesis the naturally occurring alkaloid anabasine (*20*, *20a*), isolated from *Anabasis aphylla* was found to be identical in structure with neonicotine but optically active. Anabasine has also been shown to occur in the tobacco tree, *Nicotiana glauca* (*21*), which is widely distributed in our southwestern states. A number of compounds derived from nicotine itself have also been tested. Meta-nicotine (III) is almost equal to nicotine in toxicity; dihydrometa-nicotine and nicotyrine (IV), although less toxic than meta-nicotine, still exhibited this



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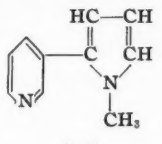
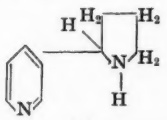


(IV)

property to a degree which far exceeded any of the purely synthetic pyridine derivatives tested (*17*). Nornicotine (V) (*18*) differs from nicotine in that the



(V)

methyl group on the nitrogen of the pyrrolidine ring has been replaced by hydrogen. It has been shown to be the predominant alkaloid of a strain or variety of ordinary tobacco, *Nicotiana tabacum* (*4*).

PYRETHRINS

The two pyrethrins are the insecticidal principles of pyrethrum belonging to the genus *Chrysanthemum*. The genus contains more than 100 species, but only

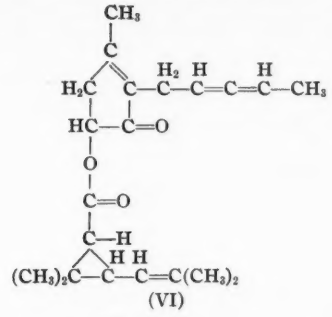
one, *Chrysanthemum cinerariaefolium*, is commercially important as an insecticide. To the casual observer *C. cinerariaefolium* resembles the ordinary daisy, but the two plants are readily distinguishable to the botanist. The fully open flowers only are used as an insecticide. They are ground finely and used as such in the form of extracts made with suitable organic solvents. The flowers can be grown in almost every state in the Union, but for economic reasons most of them are imported. Until August, 1940, about 90 per cent of the annual imports (Table 1) came from Japan, the remainder from Dalmatia, France, and Kenya Colony, Africa. Since that time Kenya flowers have largely superseded those from Japan.

TABLE 1

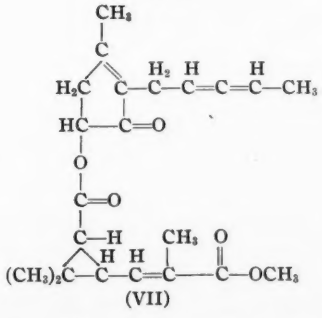
IMPORTS OF PYRETHRUM INTO THE UNITED STATES

1930	8,500,000
1931	4,500,000
1932	12,100,000
1933	10,400,000
1934	10,600,000
1935	15,600,000
1936	11,750,000
1937	20,000,000
1938	14,500,000
1939	13,500,000
1940	12,600,000

The insecticidal properties of pyrethrum are due to two high-boiling, viscous liquids termed pyrethrin I ($C_{21}H_{28}O_3$) (VI) and pyrethrin II ($C_{22}H_{28}O_5$) (VII). They are esters of a cyclic ketone alcohol, pyrethrolone, and two acids, chrysanthemum monocarboxylic acid and chrysanthemum dicarboxylic acid methyl ester.

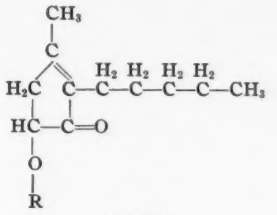


(VI)



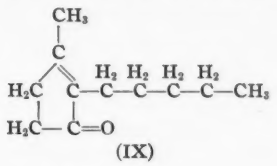
(VII)

The structures assigned are largely due to the splendid work of Staudinger and Ruzicka (*22*). The presence of an allene or cumulated system of double bonds in the five-carbon side chain was supported by the studies of LaForge and Haller (*23*). They also showed (*24*) the presence of a double bond in the alpha-beta position with respect to the carbonyl group of pyrethrolone in place of two hydrogen atoms proposed in the original formula. Both the pyrethrins are rapidly hydrogenated with the formation of tetrahydro derivatives (VIII) (*25*). When the absorption of hydrogen is prolonged, cleavage of the molecule takes place (*26*). Pyrethrin I yields tetrahydropyrethrone (IX) and dihydrochrysanthemum monocarboxylic acid and pyrethrin II gives tetrahydropyrethrone and chrysanthemum dicarboxylic acid methyl ester. Tetrahydropyrethrone has been shown to be identical with the dihydro derivative of jasmone (X) (*27*, *28*), a perfume; thus it is possible to obtain a perfume from an insecticide. The hydrogenation of the pyrethrins with the formation of acid has been made the basis of a method for their determination (*29*).

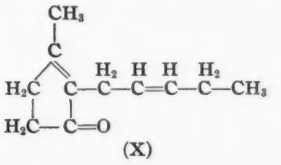


(VIII)

(R represents the acid radicals of formulas VI and VII.)



(IX)



(X)

Minor changes in the pyrethrin structures destroy for the greater part their insecticidal properties. Both of the tetrahydropyrethrins are relatively non-toxic to houseflies (*30*). Condensation of pyrethrolone with acids other than the chrysanthemum acids or esterification of the chrysanthemum acids with alcohols closely related to pyrethrolone as well as with other alcohols yielded products that were without effect or were only slightly toxic to cockroaches (*31*, *32*). Most of the studies with derivatives and closely related compounds indicate that the characteristic insecticidal action of the pyrethrins is to be attributed to the molecule as a whole rather than to some component parts.

ROTENONE AND RELATED COMPOUNDS

Rotenone, deguelin, toxicarol, sumatrol, elliptone, and malaccol are the principal insecticides in a group of

plants belonging to the *Fabaceae* family (*33*). *Derris* and *Lonchocarpus* are the most important genera commercially. The former is obtained from British Malaya and the Dutch East Indies and the latter from

Courtesy of U. S. Department of Agriculture, Bureau of Entomology and Plant Quarantine

POWER SPRAYER

Showing arrangement of nozzles for spraying rowed crops where it is essential to spray only tops of plants

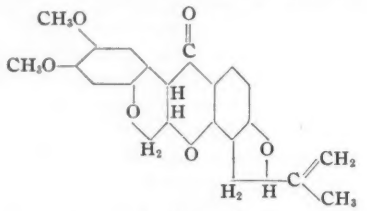
South America. The insecticidal properties of these roots have been known for a long time, but only during the past ten years or so have they been used in commercial quantities. In 1940 more than $6^1/_2$ million pounds of *Derris* and *Lonchocarpus* were imported into the United States. Imports during the past ten years are shown in Table 2.

TABLE 2

IMPORTS OF *Derris* AND *Lonchocarpus* INTO THE UNITED STATES

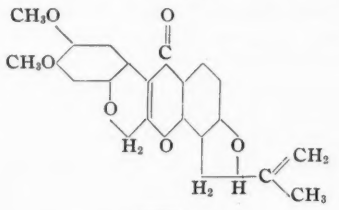
Year	*Derris, Pounds*	*Lonchocarpus, Pounds*
1931	4,500	3,900
1932	40,000	11,900
1934	100,000	500,000
1936	510,000	1,700,000
1938	750,000	2,300,000
1939	2,400,000	2,750,000
1940	3,200,000	3,350,000

Rotenone, a colorless, crystalline solid having the molecular formula $C_{23}H_{22}O_6$, is probably the most important insecticidal constituent in these plants. It has been shown to have the structural formula (XI) (*34*). This

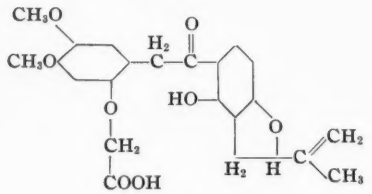


(XI)

formula consists of three characteristic systems, a central dihydro-γ-pyrone combined on the one hand with a dihydrobenzopyran and on the other with a dihydrobenzofuran system. One of the reactions of rotenone common to all of the closely related compounds, such as deguelin, etc., is the loss of two hydrogen atoms on gentle oxidation with the formation of dehydro derivative (XII) (*35*). On treatment with

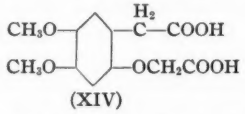


(XII)

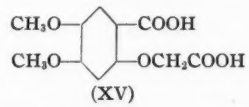


(XIII)

alcoholic potash this compound adds two molecules of water to form derrisic acid (XIII) (*35*), which when oxidized with hydrogen peroxide yields derric acid

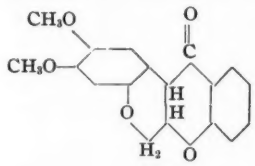


(XIV)



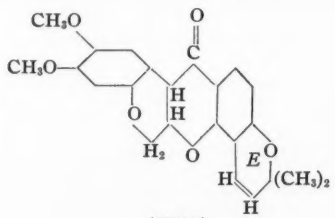
(XV)

(XIV) (*36*). With potassium permanganate derric acid yields a lower homolog, risic acid (XV) (*37*). This sequence of reactions is shown by all the compounds having a chromane–chromanone ring system (XVI).



(XVI)

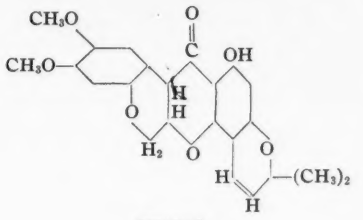
Deguelin (*38*), isomeric with rotenone, has been shown to have the structural formula (XVII). It differs from



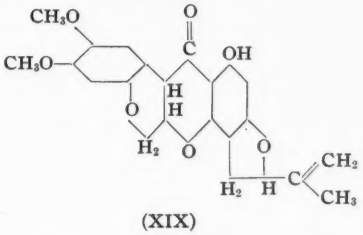
(XVII)

rotenone in that ring *E* is a substituted chromene, whereas in rotenone it is a substituted dihydrofuran. Unlike all the other compounds of this group, the optically active form of deguelin has not yet been obtained in crystalline form, although evidence has been

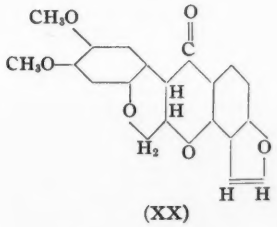
presented that it occurs in the root in a levo-rotatory form (*39*). Toxicarol (XVIII), $C_{23}H_{22}O_7$, is a hydroxydeguelin (*40*). As ordinarily isolated toxicarol is optically inactive, but the naturally occurring form levo-α-toxicarol has been obtained in crystalline form (*41*). Sumatrol, $C_{23}H_{22}O_7$ (*42*), has been shown to have the structural formula (XIX) and may be regarded as a hydroxyrotenone. Elliptone has the molecular formula $C_{20}H_{16}O_6$ (*43*). Its structure has been shown to be represented by (XX). Malaccol, $C_{20}H_{16}O_7$ (*44, 45*), may be regarded as a hydroxyelliptone (XXI). Malaccol bears the same structural relation to elliptone as sumatrol to rotenone and toxicarol to deguelin.



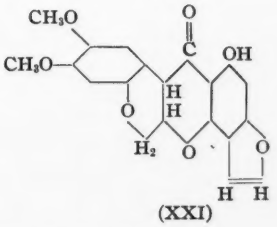
(XVIII)



(XIX)



(XX)



(XXI)

The rotenone-bearing plants have been shown to be toxic to many widely different species of insects (*46*). McIndoo, Sievers, and Abbott (*47*), in an extensive study of derris as an insecticide, have demonstrated that it acts both as a contact and as a stomach poison. In Table 3 the relative toxicity to insects of rotenone and some of the related compounds is given. It will be noted that in this series of compounds, as in nicotine and related compounds, optical activity plays an important role in insecticidal action.

TABLE 3

RELATIVE TOXICITY TO INSECTS OF ROTENONE AND ALLIED SUBSTANCES
(Toxicity of Rotenone Taken as 100)

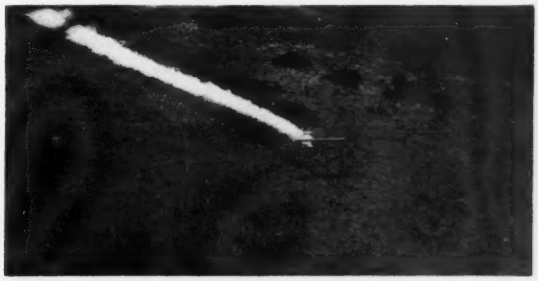
Substance	*Approximate Relative Toxicity*	*Test Insect and Reference*
Rotenone	100	.....
Deguelin (inactive)	10	Bean aphid (*Aphis rumicis* L.) (*48*)
	10	Housefly (*Musca domestica* L.) (*49*)
	30	Silkworm (*Bombyx mori* L.) (*50*)
Deguelin concentrate (active)	50	Housefly (*Musca domestica* L.) (*49*)
Tephrosin (inactive)	2	Bean aphid (*Aphis rumicis* L.) (*48*)
	10	Silkworm (*Bombyx mori* L.) (*50*)
Toxicarol (inactive)	<1	Bean aphid (*Aphis rumicis* L.) (*48*)
Toxicarol (active)	7	Bean aphid (*Aphis rumicis* L.) (*51*)
Sumatrol (active)	7	Bean aphid (*Aphis rumicis* L.) (*51*)
Dihydrorotenone (active)	70	Housefly (*Musca domestica* L.) (*49*)
	>30	Silkworm (*Bombyx mori* L.) (*50*)
Dihydrodeguelin (inactive)	<3	Housefly (*Musca domestica* L.) (*49*)
Dihydrodeguelin (active)	50	Housefly (*Musca domestica* L.) (*49*)
Dehydrorotenone (active)	0	Imported cabbage worm (*Ascia rapae* (L.)) (*52*)

Sumatrol, malaccol, and elliptone occur in the roots in only small amounts, and sufficient work has not yet been done to compare their insecticidal value with rotenone.

Many derivatives of rotenone and degradation products have been tested as insecticides, but only dihydrorotenone (*53*), in which the double bond of the side chain has been saturated, is of the same order of toxicity as rotenone (*49*). Rotenonic acid (isodihydrorotenone) (*53*), which is formed by hydrogen cleavage of the furan oxygen and usually accompanies the preparation of dihydrorotenone, is relatively non-toxic to insects.

HELLEBORE ALKALOIDS

Hellebore is the common name for plants belonging to the lily family (*Liliaceae*) and the genus *Veratrum*. Green hellebore, American white hellebore, and American false hellebore are common names for *Veratrum viride*. The closely related European species *V. album*, which is the source of powdered commercial hellebore, is commonly called white hellebore. The toxicity of



Courtesy of U. S. Department of Agriculture, Bureau of Entomology and Plant Quarantine

AIRPLANE DUSTING ON LAKE FOR MOSQUITO CONTROL

both *Veratrum* species, long used as insecticides, has been shown to be due to alkaloids belonging to a class known as the veratrin alkaloids (*1, 54*). Several alkaloids have been isolated and all possess complicated

structures. Recently there has been a renewed interest in the chemistry of them (*55*) and in the insecticidal properties of hellebore (*54*). That not all the alkaloids present in *V. viride* are insecticidal was shown by separating the alkaloids into an ether-soluble and an ether-insoluble fraction. The former was about five times more toxic to the American cockroach than was arsenic trioxide, and the ether-insoluble fraction was not toxic to this insect.

U. S. Department of Agriculture Photograph by Purdy

ROOTS OF THE THUNDER GOD VINE GROWING AT GLENN DALE, MARYLAND, FROM CUTTINGS OBTAINED BY A PLANT EXPLORER OF THE U. S. DEPARTMENT OF AGRICULTURE

With these roots, chemists and entomologists of the Department have prepared an insecticide, which they are now testing to find out whether or not it can be used here as it is in China, as a protection to market garden crops.

QUASSIA

Extracts of quassia wood have been used for many years for insecticidal purposes. The original source of quassia wood or chips was the Surinam quassia (*Quassia amara*), a small branching tree or shrub of the family *Sumarubaceae*, but this has been displaced to a large extent by Jamaica quassia (*Aeschrion excelsa*) of the same family.

According to McIndoo and Sievers (*56*) the first authentic record of the use of extracts of the wood as an insecticide is that by Ormerod (*57*), who found the water extract to be effective against the hop aphid. From a detailed study of quassia McIndoo and Sievers (*56*) concluded that owing to its poor insecticidal properties quassia would not become a general insecticide for all aphids. However, pests other than aphids have been successfully controlled by quassia. A brief summary of the insects thus controlled is given by Holman (*58, 58a*).

Recently a renewed chemical study of quassia and related materials has been undertaken by Clark (*59*). He has isolated in pure form several crystalline bitter principles. However, tests against several species of insects have shown them to be relatively non-toxic (*60*).

It perhaps should be reiterated that the foregoing account covers only those plant materials that have found commercial application as insecticides. While a large number of plants (*1, 3*) have been tested for insecticidal properties and chemical studies have been made on some of them, a large field remains unexplored. As pointed out by Roark (*61*), many plants have been only superficially studied. The fact that an organic compound may be highly toxic to one insect and relatively non-toxic to another makes it necessary to evaluate materials against a number of species of insects. Finally, it may be pointed out that, while the naturally occurring insecticides discussed above possess complicated structures and there is little hope for their synthesis in the chemical laboratory at this time, molecules possessing complicated structures, *per se*, are not necessary for insecticidal properties. Hydrogen cyanide, methyl bromide, ethylene oxide, ethylene dichloride, dichloroethyl ether, alkyl and aryl thiocyanates, and many other relatively simple compounds might be cited as examples of compounds that are valuable in the control of insect pests. The availability during the past fifteen years of many synthetic organic compounds for industrial use has stimulated research on these materials as insecticides, and a large number of compounds unrelated to plant products have been tested. A discussion of them at this time is beyond the scope of this paper.

Cracca virginiana IN BLOOM

Illustrating a native plant that shows promise as a source of insecticides

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QUALITATIVE DETERMINATION OF FERROCYANIDE ION WITH QUINONE CHLOROIMIDE

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THE usual tests for ferrocyanide ion involve the use of uranyl acetate, ferric chloride (*1*), and titanium tetrachloride (*2*). The few organic reagents recorded in the literature include quinoline hydrochloride, benzidine hydrochloride, and indigo carmine (*3*).

It has been found that quinone chloroimide (0 : C_6H_4: NCl) gives a characteristic color reaction with ferrocyanide ion, permitting positive identification of the latter either alone or in the presence of ferricyanide ion. The presence of strong oxidizing agents interferes with the test.

The alcoholic quinone chloroimide solution darkens on standing and should be freshly prepared for use immediately prior to making the test.

PROCEDURE

Prepare a 0.5 per cent solution of quinone chloroimide[1] in ethyl alcohol.

[1] Quinone chloroimide, Eastman Practical, m. p. 75°–78°C. (Purified by steam distillation.)

Place 0.5 ml. of the neutral or slightly acid solution under test in a depression of a white porcelain spot test plate. Add 5 drops of the 0.5 per cent alcoholic quinone chloroimide solution. In the presence of ferrocyanide ion an emerald green color will develop in 15 to 30 seconds. Stronger concentrations of test reagent and test solution result in the formation of a dark brown precipitate.

When carried out in this manner the test will detect 5 γ of potassium ferrocyanide.

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The Construction of an Emergency Civilian Gas Mask

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CIVILIAN gas masks are not likely to be supplied in any large quantity for some months to come, and until then the public either will have no protection against gas attacks, or they may provide themselves with some degree of protection by constructing their own masks. Surprise is a vital factor in air attack and preparedness is the best defense. Not only would homemade masks afford protection, but the greater the number of civilians in possession of gas masks at the earliest possible date, the less likelihood of an enemy gas attack.

This paper describes the construction of a nearly rubberless emergency mask from cheap, non-critical materials, and using the facilities ordinarily available at home or in the typical high-school laboratory. It should be observed, however, that no mask may be offered for sale without formal approval of the Government.

A civilian gas mask may be simpler in design than a service mask because there is an essential difference in their purposes. The service mask must enable the wearer to remain and work in a contaminated area, whereas a civilian mask need only afford protection sufficient to allow the wearer to escape from a contaminated area or to remain until assistance arrives or the emergency is past. The mask described herewith, therefore, was designed to protect eyes and lungs against typical war gases such as mustard, chlorpicrin, chlorine, and others for several hours. This should be ample time for a civilian to escape several miles from a bombed area, even though he walks slowly.

Should a person use the emergency mask during a gas attack, the charcoal should either be replaced with new, or the spent charcoal regenerated by heating to 300°C. or over, for several minutes under conditions which would allow escape of the fumes up a chimney.

The emergency mask is made in two parts: gasproof goggles and the charcoal respirator unit which fits over the nose and mouth. This type of construction not only simplifies the design but greatly extends the range of materials that may be used.

The two-piece mask has the disadvantage of fitting only the person for whom it was made. But notwithstanding this and other disadvantages of the two-piece mask, one feature in its favor is greater comfort in the summer when gas attacks are more probable.

GASPROOF GOGGLES

The object is to incorporate in each lens cavity of the goggles a quantity of active charcoal sufficient to absorb any mustard or other gas that may leak in. Eyes are far more sensitive than lungs to mustard gas. The quantity of charcoal required for each lens cavity is about a thimbleful, as has been determined by a two-hour test in chlorpicrin.

Place a piece of adhesive cellophane tape on a table, the adhesive surface uppermost. The tape is preferably $^3/_8$ inch wide, and about 14 inches long. Cover the tape with 8- to 14-mesh active charcoal and then lightly shake off any non-adherent grains. Sections of this active charcoal-coated tape are used in the lens cavities of the goggles but the manner or use depends upon the construction of the goggles.

In a common type of goggles such as "underwater," tourist, and "harvester" goggles, the lenses are set in metal frames which project from the covering. The charcoal-covered tape may be placed around the inside surface of each metal frame with the cellophane surface in contact with the metal. Only one layer of tape is necessary and it may be anchored in place with several short strips of cellophane adhesive tape.

In another type of goggles, such as welder's or motorcyclist's goggles, the lenses are molded in a resin-form which fits tightly around the eyes. Each lens cavity is large enough to contain a 6-inch strip of charcoal-coated tape rolled into a coil and anchored in place with either cloth or cellophane adhesive tape.

If the goggles contain ventilator ports they should be sealed with tape. Also, if the goggles do not fit the contour of the face snugly, they should be built up with a filler such as plastic wood or successive layers of adhesive tape until a good fit is obtained.

THE CHARCOAL RESPIRATOR

Although there are many minor features to consider in the design of a respirator, the necessary specifications are few. The respirator should offer low resistance to breathing; it should be leakproof so that air may enter only through the charcoal filter; exhaled breath should not come in contact with the charcoal. (Moisture condensed from the exhaled breath would quickly saturate the charcoal.)

Figure 1 shows the completed respirator. Two nested 8-oz. hot-liquid paper cups form the body of the mask, and they are notched to fit over nose and mouth. Inserted in the cups is a small-sized (6 oz.) condensed milk can which contains the active charcoal. One flap valve is attached to the can and another to the paper cup. Elastic bands attached with adhesive tape go around the head and hold the mask tightly against the face. Details for the construction are as follows:

1. Remove the bottoms from the two paper cups by splitting the glue joint on the inside of the cup; push

the bottom inward and straighten out the crimp. Glue one cup tightly inside the other.

2. Place a small-sized condensed milk can inside the cup and draw a pencil line around the inside wall just below the can. With scissors or tin snips make a series of cuts about 3/8 inch apart around the bottom edge of the cup up to the pencil line as illustrated in Figure 2,

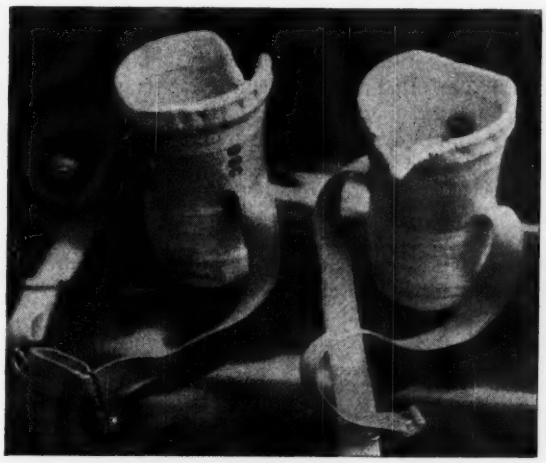

FIGURE 1.—CHARCOAL RESPIRATOR

point 10. Bend the "fins" outward so that the milk can may subsequently be inserted into the cup *from the bottom*.

3. With a handle made of wire, ribbon, or tape twisted around the milk can near the bottom, hold the lid in a flame until the solder around the rim of the lid is melted, and "scrape" the lid off the can. Close the holes which were punched for extracting the milk, using solder and small metal patches if necessary. Avoid addition of solder to the inside surface of the rim.

Place the lid on the end of a piece of wood clamped in a vise, and with a small nail punch 75 to 100 holes 1/16 inch in diameter in the lid, confining the punched area to a concentric circle of 7/8 inch in radius.

4. Remove any remains of the label from the can and at the center of the bottom punch and ream a hole about 3/8 inch in diameter. Over this hole solder a piece of tubing (brass, copper, or iron) 3/8 inch in inside diameter and 1/2 inch long. Solder a 7/8-inch washer concentrically to the other end of this tube, to serve as a flat flange.

5. Place either a one-inch square piece of oilcloth or flat sheet-rubber (tire patch) on the washer mentioned in item 4. With a needle pass a thread downward through one corner of this patch; wrap the thread twice around the stud of tubing joining the washer to the can, placing the windings close to the washer; bring the thread back up through the patch at the same corner from which the thread started. Secure both ends of the thread. Repeat this operation at each of the remaining corners of the patch. The threads should be drawn tightly enough so that the patch will be under no constraint, yet remain in contact with the washer when held in any position. This valve if properly constructed will allow only one-way passage of air through the can and valve, respectively. If the valve makes a fluttering noise when air passes through it, tighten the binding at one corner.

6. Place the perforated lid on the can; wrap the can side-wall with one layer of tire tape (electrician's friction tape). Trim off any protruding edge of tape. Paint furniture enamel (white if desired) over the tape; coat the paper cup, inside and out, with enamel; push the can (valve end foremost) into the "finned" end of the paper cups until the can extends a little beyond the ends of the cuts; wrap string or heavy thread around the fins to clamp them tightly against the can and cause the wet enamel to ooze into the cuts between the fins; fill the small crevice between the can and the inside wall of the cup with a little extra enamel; allow the enamel to dry overnight. For the sake of appearance the perforated lid also may be enameled, but the perforations must not be filled.

7. With tin snips cut a V-notch about 1 1/2 inches deep and 1 inch wide in the rim of the cup. Opposite the V-notch cut a shallow notch about 2 inches wide and 1/2 inch deep in the rim. Place the shallow notch just below the lips, and the nose into the V-notch. With the aid of a mirror determine whether these notches should be widened or deepened in order that the cup will make contact with the face at every point. Trim the notches accordingly and test for tightness of fit by covering the perforated lid with the hand and attempting to inhale or exhale the breath. When a fairly good degree of fit is obtained, cover the edge of the cups with waterproof adhesive tape, using short strips 1/2 inch wide and about 2 inches long, stuck first on the inside of the cup, up over the edge, and down on the outside of the cup. Final precision of fit can be made by using adhesive tape to build up any section not making good contact with the face. Figure 2 illustrates the type of notches to be cut; Figure 1 shows their correct position.

For a small face the 8-oz. cups may be too large in diameter. In that case reduce the diameter by inserting two nested 6-oz. cups glued together and wrapped with enamel-wet string until a tight fit within the larger cup is obtained. The smaller cups should project above the rim of the larger cup. Cut the notches in the smaller cups.

8. Prepare another flap-valve as described in item 4, but solder the washer to a piece of threaded tubing instead of plain tubing. A 3/8-inch × 1/2-inch brass nipple, generally obtainable where electric lamp shade parts are sold, is excellent for this purpose. Two thin nuts to fit the nipple are required.

9. Cut a hole (preferably with a cork-borer) directly below the chin notch in the wall of the paper cups to fit the nipple section of the second flap-valve; insert the nipple in this hole and with the aid of the two nuts on

opposite sides of the cup, clamp it tightly in place with the flap-valve outside.

10. Elastic headbands are attached to opposite sides of the mask by a generous wrapping of adhesive tape. The bands are laid directly over the thread which binds the paper fins to the tin can, and set at a slight angle so that the bands will be straight when placed around the head. A pair of $^3/_4$-inch adjustable garters with hook connections will serve. Should elastic be unobtainable use wide ribbons long enough to be crossed at the back of the head and tied at the forehead.

These operations complete the construction of the mask and there remains only the filling of the can. The filling consists of one ounce of active charcoal (described below) sandwiched between layers of dry steel wool, with a top and bottom layer of copper (or steel) wool wet with a glycerin preparation. Although steel wool may be used throughout if copper is unavailable, copper wool is preferred for the top and bottom layers because it can be compressed to a tighter cake by light hammering. Better removal of irritant smokes results, and the copper may retain some of the arsenicals by chemical reaction.

One steel wool pad such as is used for scouring kitchen utensils, and a copper gauze pot cleaner are recommended. The copper gauze is straightened out, "buttered" with about 20 grams of the glycerin preparation, and cut in two. Each section is folded and hammered lightly into a semiflat but highly porous cake. Place one cake in the bottom of the can as shown in Figure 2. On top of it is placed half of a dry steel wool pad (7*A*), an ounce of active charcoal (8), another layer of dry wool (7*B*), and finally the remaining glycerinated copper cake (6*B*). When the perforated lid (9) is placed on the can the wool will be compressed slightly and the charcoal will not tend to disintegrate.

The glycerin preparation is comprised of "glycerite of starch" in which is mixed a third of its weight of sodium bicarbonate (baking soda).

"Glycerite of starch" is simply glycerin thickened with starch and may be obtained from any drug store or prepared as follows:

Stir 7 grams of starch into 20 cc. of glycerin. Heat an 80-cc. portion of glycerin to 145°C. (incipient boiling for commercial glycerin which usually contains about 5 per cent water) and add *quickly* the cold starch-glycerin mixture. When cold stir 40 grams of baking soda into the mixture. The quantities specified here are easier to work with than smaller amounts, but for one gas mask only $^1/_7$ of the above preparation is required.

The top and bottom layers of copper wool are coated with this glycerin preparation in order that the solid particles of sneeze gas may be caught. Thickened glycerin must be used to avoid drain-off. The preparation has low vapor pressure and therefore cannot cause charcoal deterioration unless in direct contact with the charcoal. The dry layers of steel wool prevent this contact. The sodium bicarbonate is added to assist in removal of any hydrogen chloride which might be evolved as a result of hydrolytic reactions within the charcoal. It may also assist hydrolysis of the arsenicals.

If this mask is made and used properly, and its limitations appreciated, it can prove very useful in the event of a surprise raid. In addition, however, the construction of the mask can be justified on educational grounds alone. Training in the use of a mask is important. Supervised gas mask drill as outlined in the War Department publication FM 21-40, "Defense against Chemical Attack," would be excellent instruction even with the improvised mask. Tightness of fit, flutter valve inspection, suction test, and actual operation in a gas chamber with some odorous non-toxic gas such as butyl mercaptan or tear gas (chloracetophenone) would afford excellent training which would be of real value later when better masks are issued.

PREPARATION OF ACTIVE CHARCOAL

While active charcoal may be obtainable commercially, it is instructive to prepare it. Therefore, the following directions are given for its preparation and activation. In any event, whether purchased or homemade, its activity should be tested by the method described below, before using it.

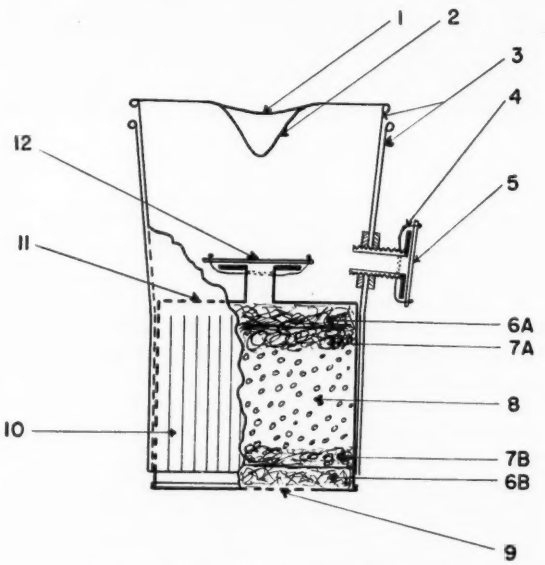

FIGURE 2.—ACTIVE CHARCOAL RESPIRATOR

1—Chin notch
2—Nose notch
3—Paper cups
4—Thread to hold flap
5—Exit flap-valve
6*A*, 6*B*—Glycerinated copper wool
7*A*, 7*B*—Dry steel wool
8—Active charcoal
9—Perforated lid
10—Paper "fins"
11—Condensed milk can
12—Intake flap-valve

This drawing shows these notches in a plane 90° from their correct positions as shown in the photograph, Figure 1.

Charcoal suitable for use in a gas mask must be granular in form and have high sorptive activity. Hardness is not absolutely necessary, but is a desirable property in order that disintegration

as a result of handling may be minimized. The two best raw materials for making gas mask charcoal are coconut shell and black walnut shell. Their resultant charcoals are nearly identical. Less desirable but nevertheless useful charcoals have been made from semihard raw materials such as peach pits, cherry stones, and Masonite Tempered Presdwood. So-called hard woods, such as oak, beech, etc., are relatively soft and are not recommended. Although they can be activated highly yields are low (5 to 10 per cent) and the charcoals crumble easily.

The activation procedure requires apparatus which will heat the charcoal *uniformly* to about 1000°C., and the attainment of this temperature becomes more difficult the larger the apparatus. It is better therefore to activate the charcoal in several small batches than to attempt to make a large quantity all at once unless one is so fortunate as to possess the necessary heating equipment.

Procedure

About 400 grams of the raw material (three dozen black walnuts, or two coconut shells) are placed in a wide container (such as a coffee can) and heated until all combustible gases have been driven off. The particular manner in which this preliminary charring is accomplished is incidental. Extinguish the embers, with water or otherwise. Nearly three-fourths of the weight of the raw material will be lost during the charring operation, and the volume shrinkage is about 30 per cent. Crush the product until all of it will pass an 8-mesh sieve (eight openings per linear inch). Some of the juice strainers on the market are of this size. Remove and discard the fine particles which pass through a 14-mesh sieve (a flour sifter or coarse window screen will do). The material held on the 14-mesh sieve is ready for the activation process.

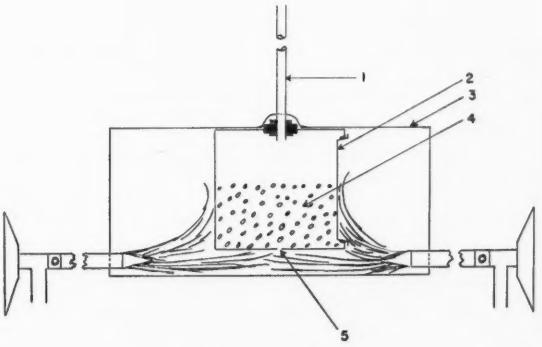

FIGURE 3.—CHARCOAL ACTIVATOR
1—Inlet tube for CO_2
2—1/4-Pint tin can
3—Sheet asbestos rolled into a tube
4—Charcoal to be activated
5—Hole for exit gases

The activating apparatus (Figure 3) may be concisely described as a "tin-can muffle furnace." The materials required are: a 1/4-pint, friction top tin can (paint is often sold in such a can); a piece of sheet asbestos (hot air furnace conduit covering) 6 inches wide, 12 inches long, and preferably 1/16 inch thick; a piece of 1/4-inch O.D. copper tubing (gasoline line) about a foot long (small iron tubing will do, or even pyrex glass but these are less convenient); two Bunsen burners; and a source of carbon dioxide.

With a small nail punch a 1/16-inch hole in the middle of the can wall. Diametrically opposite it drill or punch a larger hole and ream it to hold the 1/4-inch tube. Thread the tube at one end to take standard nuts and attach the tube to the can. Place small iron washers under each nut and a washer made from sheet asbestos adjacent to the inside wall of the can. When the nuts are tightened a heat-resistant, gastight connection will result.

Wet the asbestos sheet thoroughly and wrap it around the can loosely and eccentrically so that there will be a half-inch air space between the sheet and wall of the can opposite the place where the copper tube is attached. With the copper tube extending upward as shown in Figure 3, press the wet asbestos against the upper can wall and around the copper tube, slitting the sheet as necessary to accommodate the tube. Press the overlap of the sheet together at the outside edges and allow the wet sheet to dry; it will then retain its shape and position. Two Bunsen burners (or blow torches) are set to project their flames against opposite ends of the can and into the air space between the asbestos and the can.

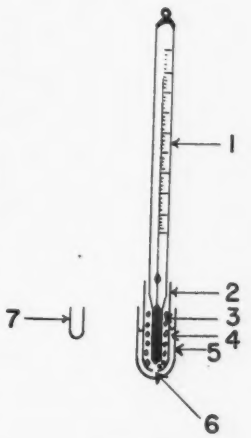

FIGURE 4.—TEMPERATURE OF WETTING APPARATUS
1—Clinical thermometer
2—No. 0 capsule (*B*)
3—Charcoal sample
4—Carbon tetrachloride
5—No. 000 capsule cap (*C*)
6—Pinhole
7—No. 1 capsule cap (*A*)

Load the can half full with a portion of the 8- to 14-mesh charcoal (about 30 grams) and press the lid on snugly. Attach the copper tube to a carbon dioxide generator and allow the gas to flow through the apparatus for a minute or two to displace the air, then light the burners and adjust them to heat at least the lower half of the can to the maximum attainable temperature (900°C. to 1000°C.). After the can has attained this temperature shut off the burners for an instant and observe the air space between the can and asbestos sheet. If all is well a small flame should be issuing from the tiny hole in the can. Relight the burners at once and continue the heat and carbon dioxide flow for about two hours.

Although not necessary, the flow of carbon dioxide is conveniently observed by bubbling the gas through water. The rate of flow should be a little too fast for the bubbles to be counted. Cylinder carbon dioxide is the handiest source but a Kipp generator may be used. Or, one may fill a medium-sized oil can with dry ice and attach the spout to the copper tube of the tin-can activator. Regulate the flow of carbon dioxide by wrapping absorbent cotton around the oil can. Two ounces of dry ice in the oil can will require about an hour to evaporate, at the end of which time refilling will be necessary. If dry ice is unavailable, fill the oil can half full with baking soda and heat it with a flame.

At the end of two hours, turn off the heat and allow the charcoal to cool with the carbon dioxide still flowing. When cold remove the charcoal and weigh it. If a third to half of the original charcoal has been consumed in the activation process, high activity is indicated. Test it qualitatively by placing a small quantity (0.1 to 0.2 gram) in the palm of the hand and adding about five drops of carbon tetrachloride. If the charcoal gets warm it is sufficiently active to be tested further. If not, replace the charcoal in the can and continue the activation process until the qualitative test gives a positive result.

Steam may be substituted for carbon dioxide in this process, since for activation purposes these gases are equivalent, as was pointed out by Ostrejko.[1] However, should this substitution be made, the possibility of an explosion due to hydrogen generation should be appreciated.

The apparatus described above will produce about 20 grams of active charcoal per batch. About 35 grams will be required for

[1] Ostrejko, U. S. Patent 739,104; Ger. Patent 136,792. XII d (1902).

the respirator and goggles and therefore the activation step as outlined above must be performed twice. If larger heating equipment is available a half-pint can may be used and all of the charcoal activated in one batch.

A Rapid Test for Charcoal Activity

A determination of the heat of wetting is well recognized as a reliable method for the estimation of charcoal activity, and precise calorimetric data afford an accurate measure of the activity. When a degree of accuracy sufficient to inform one whether a given sample of charcoal is active enough for safe use in a gas mask is all that is required, less elaborate apparatus may be used and only the temperature of wetting under empirical but constant conditions need be observed. The temperature of wetting has therefore been made the basis for the following test.

The materials required are: a clinical thermometer, medicine dropper, carbon tetrachloride, and three gelatin capsules, sizes No. 000, No. 0, and No. 1.

Discard the cap from the No. 0 capsule and puncture the base of the remaining portion with a pin. Call this punctured container *B*. Save only the caps from the No. 000 and No. 1 capsules and call them *C* and *A*, respectively. *A* is used for measuring the quantity of sample to be tested.

Fill *A* level-full with the sample and dump it into *B*, as shown in Figure 4. Shake down the mercury in the clinical thermometer until the reading is somewhere below 100°F. Insert the thermometer in *B* until the bulb touches the bottom. Tap gently so that the charcoal will surround the bulb compactly. Place 20 drops of carbon tetrachloride in *C* (the largest capsule cap); lower *B* into the carbon tetrachloride carefully (to prevent overrun); wiggle the thermometer around to assist rapid wetting but avoid raising it from the bottom of *B:* after about 20 seconds read the thermometer.

The capsules may be used repeatedly, and the test requires about one minute to perform.

In ten consecutive tests made on a coconut charcoal sample having a chlorpicrin activity of 60 minutes, the average temperature of wetting under the above conditions was 109°F. The lowest reading was 108.4°F. and the maximum was 110°F. Similarly, a sample having a chlorpicrin activity of 41 minutes registered an average wetting temperature of 104.6°F.

Merck's "Medicinal Charcoal," a powdered charcoal probably made from blood and commonly used for decolorizing liquids, was found to have an average wetting temperature of 102.5°F., which would correspond to a chlorpicrin activity, estimated from the preceding data, of about 30 minutes. A quantity of it was pelleted and tested by the standard chlorpicrin method. Its activity on the chlorpicrin scale was found to be 29 minutes.

These data show that the above procedure affords a reliable method for estimating the activity of charcoal intended for use in a gas mask, and a charcoal of appropriate hardness and particle size, showing (average of five determinations) a wetting temperature of 103°F. or better, may be considered active enough for use in the emergency gas mask.

What's Been Going On

(*Continued from page 302.*)

been more widespread. The adoption of some fairly comprehensive plan of deferment for occupational training would be helpful.

2. *Financial aid to qualified youth.* Youth with high mental ability should be financially aided to continue their education. The federal government should provide the funds to the individual youth if necessary. Money should not be an obstacle in the acquisition of the most necessary resource for the war effort—trained men to plan and produce the materials on which victory depends. Such financial aid also might be the deciding factor to a youth who is trying to choose between continuing his education and taking an industrial job. If he were assured that he could continue his education he would probably accept the temporary lower scale of living that continuance of higher education offers as opposed to the affluence of high wages from industry. It may be that institutions should assist in a program of providing professionally trained manpower for the fields in which the greatest shortages exist by turning all funds available for scholarships to defrayal of expenses of youth with known aptitudes for these fields.

3. *Stimulation of secondary-school students to enter fields in which shortages exist.* Since many American colleges draw a majority of their students from neighboring areas within a radius of 100 miles, it should not be an impossible task for a college staff to keep a fairly close check on the qualifications, aptitudes, and abilities of the boys and girls in all secondary schools in its area. In this way guidance toward professions in which shortages exist could be started in the early years of secondary education. Probably no more than 10 per cent of the secondary schools of the nation have skilled guidance counselors. Without guidance and stimulation, it is easy for a talent in chemical research to be submerged under the acceptance by family and student that Johnny will become a lawyer or banker. One college administrator, in listing the facilities of his college, noted that his institution was equipped both with materials and staff for teaching of sciences to far more students than enrolled. He suggested that it might be possible to open the laboratories to high-school students from neighboring communities; or at least to furnish the staff for teaching laboratory technics to high-school students. Such an experiment might uncover aptitudes among youth that otherwise would go unnoticed. Through the consequent interest and curiosity, these youth might be stimulated into pursuing higher education.

4. *More careful counseling of women matriculants.* Although the number of women students in institutions of higher learning has risen steadily during the century, the survey shows that of the 172,000 graduates who will leave college this year, either as graduates or postgraduates, roughly one-third will be women. The distribution of two men graduates to one woman graduate is not consistent even within the occupational fields, however. Only in medicine and related fields (including nutrition and nursing) is this ratio approximated. In the physical sciences, men outnumber women 5 to 1; in engineering, almost 600 to 1; in clergy, the ratio is 27 to 1; in management and administration, the ratio drops to 6 to 1; and in agriculture and biology, it is 3 to 1. Only in arts and languages do women outnumber men (2 to 1); in the social sciences the numbers are approximately equal. If women would take up studies in the occupations at present greatly undermanned, a great potential pool of workers would be established.

A synthetic resin treatment gives nails a protective coating which serves the same purposes as galvanized dipping, without using metals needed for defense. These nails are rustproof, hold onto wood with the tenacity of galvanized nails, and are not toxic or obnoxious to workers putting nails in their mouths on the job.

—LAUCKS

A New Precipitant for Group II Ions

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A NUMBER of attempts have been made to find some method that would permit the separation of the metallic ions into groups without resorting to gaseous hydrogen sulfide. A good summary and an excellent bibliography of the history of the problem may be found in a paper by Cornog.[1] During the past few years the author has tried a number of compounds containing a potential sulfide ion, among them ammonium sulfide, thioacetic acid, thiourea, and sodium diethyl dithio carbamate, compounds which had been suggested by other workers in the field. These were unsatisfactory for various reasons. In addition to these sulfur compounds which had been previously proposed we tried a number of organic bases for the purpose of adsorbing gaseous hydrogen sulfide in the hope that a salt would be formed, stable enough to permit its use as a precipitant for Group II ions. However, all of the bases tried proved to be either so weakly basic that no stable salt could be formed, or so strongly basic that the salt, upon hydrolysis, would cause a concurrent precipitation of Group III ions.

Early in 1941 there was brought to our attention a new type of resin which has the property of adsorbing anions. This suggested that the resin might have the ability to adsorb hydrogen sulfide, which proved to be true. Since the substance thus formed seemed to be quite stable, its use as a precipitant for Group II ions was tried. With a few modifications in the regular procedure, the resin saturated with hydrogen sulfide proved to be a very satisfactory substitute for the gaseous hydrogen sulfide.

THE RESIN

The resin used is of the amine-formaldehyde condensation type, and is known commercially as IR-4. The properties of this resin have been thoroughly discussed in a recent article by Myers, Eastes, and Myers.[2]

The Amberlite IR-4 is a brown solid, which is sold in a light, flaky, granular form, and has the appearance of sawdust. If just enough water is added to form a slurry, adsorption of hydrogen sulfide is rapid. This is most conveniently accomplished by placing the moistened Amberlite IR-4 in a one-liter flask provided with a one-holed stopper through which a glass tube runs almost to the bottom of the flask. After all the air in the flask has been displaced by bubbling in H_2S, the stopper is placed in the flask and the H_2S allowed to bubble in without further supervision. It is possible to hasten the adsorption of the gas by agitation, but complete adsorption can be obtained with less trouble by leaving the IR-4 in contact with the H_2S for several days with only occasional agitation. The resin adsorbs 12 per cent of its weight of H_2S.

The product formed is quite stable if kept in tightly stoppered flasks or test tubes. Samples of the resin, saturated with H_2S, have been kept for eight months without any indication of decomposition. Decomposition may be easily detected, since the rich green color of the saturated resin changes back to the original brown upon the loss of the H_2S.

For simplicity in use as a Group II precipitant, it has been found desirable to place the saturated resin in a number of tightly stoppered 20-ml. test tubes immediately after its preparation. One of these tubes is used to fill six 3-ml. test tubes, also tightly stoppered. Each of the 3-ml. tubes holds enough of the resin for seven or eight semimicro analyses. With this procedure there is practically no decomposition of the precipitant, since the amount in the small 3-ml. tube is quickly used up. The large 20-ml. tubes need be opened but once, to fill the smaller tubes.

PROCEDURE FOR SEMIMICRO ANALYSIS

The filtrate from Group I is evaporated to dryness, moistened with a drop of concentrated HNO_3, evaporated to dryness again, and then dissolved in 4 ml. of 0.35 *N* HCl. To this solution are added approximately 400 mg. of the precipitant and the mixture is then placed in a boiling water bath for 10 minutes. The solution is then filtered and the residue washed with a one-ml. portion of 0.35 *N* HCl. The filtrate contains the Group III cations; the residue consists of the sulfides of the Group II cations. The residue, consisting of exhausted resin and the sulfide precipitate, is leached with warm sodium polysulfide solution for about three minutes, filtered, and washed. The filtrate will contain the soluble complex thio salts of mercury, tin, antimony, and arsenic; the residue will contain the resin and the sulfides of copper, lead, bismuth, and cadmium. The residue is treated with 2 ml. of 4 *N* HNO_3 and heated on a boiling water bath for five minutes. This leaching is repeated with another one-ml. portion of the HNO_3. Filter and wash with one ml. of 6 *N* H_2SO_4. (The H_2SO_4 is used to prevent any precipitation of remaining bismuth ions as the basic sulfate and also to furnish the necessary sulfate ions for the subsequent removal of the lead as lead sulfate.) After this leaching with the nitric acid the resin can be discarded. The filtrate contains the copper subgroup, but some of the resin dissolves in the hot HNO_3 and imparts a deep orange color to the solution when it is made basic by the addition of ammonium hydroxide for the copper test. This orange color obscures the blue color of the copper complex so that a supplementary test for copper becomes necessary.

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SUPPLEMENTARY NOTES

For satisfactory results by beginning students, 2 mg. of any individual ion should be present per ml. of unknown solution, although some ions can be used in smaller amounts (Cu, 0.4 mg.; As, 0.5 mg.; Pb or Bi, one mg.). Assuming a maximum total of 15 mg. present, 4 to 6 mg. of sulfide ion will be ample for precipitation. The amount of precipitant recommended in the procedure, if saturated, will yield about 46 mg. of potential sulfide ion, insuring the considerable excess generally recommended for Group II separations.

The use of too much of the resin may result in the acidity being lowered to the point where Group III may be precipitated. By using the amount and the conditions stated, a titration showed that the acidity was lowered from the original 0.35 normality of the HCl to 0.07 *N*. Despite this reduction in acidity there is no co-precipitation of the Group III cations at the time at which the Group II cations are being precipitated. This was proved by the analysis of a great number of known mixtures of Group II and Group III cations.

The possibility of precipitation of Group III was also investigated experimentally by using 10-mg. samples of each of the Group III cations.

Each of these samples was put through the above procedure and after filtering off the solid resin a few drops of NH_4OH and 5 drops of $(NH_4)_2S$ solution were added to the filtrate. Another 10-mg. sample of each cation was precipitated directly with NH_4OH and $(NH_4)_2S$, without previous addition of the Group II precipitant. The corresponding pairs of precipitates were centrifuged under identical conditions and the amounts of precipitate compared. Only in the case of aluminum was there any perceptible difference, and then only about 20 per cent.

From these results it seems safe to conclude that the possibility of co-precipitation of Group III ions during the precipitation of Group II ions is not great—at least not enough to invalidate the method.

Each of the Group II cations was studied to find the maximum amount which could be precipitated by the method outlined. Increasing weighed amounts (in 5-mg. increments, up to 25 mg.) were put through the procedure. The "Group III filtrate" was tested for complete precipitation by adding a few drops of NH_4OH and 5 drops of $(NH_4)_2S$ solution.

Maximum amounts precipitated were as follows:

Copper	8 mg.
Cadmium	14 mg.
Bismuth	More than 25 mg.
Lead	More than the amount occurring in Group II unknowns[3]
Mercury	More than 25 mg.
Tin	22 mg.
Arsenious arsenic	16 mg.
Antimony	11 mg.

In testing for the tin, arsenic, and antimony present in the filtrate it was not possible, of course, to add the ammonium sulfide. For these ions the test on the filtrate was made by bubbling hydrogen sulfide gas into the slightly acid solution. The author has used unknowns containing as much as 32 mg. of Group II cations and has obtained complete precipitation.

An interesting phenomenon which occurs during the treatment of the unknown with the precipitant is the adsorption of the phosphate ion.

Increasing, weighed amounts of phosphate were treated with the saturated resin, according to the outlined procedure, and the filtrate tested for phosphate by evaporating to dryness, redissolving, acidifying with HNO_3, and treating with 10 drops of ammonium molybdate solution. Such a semiquantitative determination showed that 8 mg. of phosphate were adsorbed under the conditions of the procedure. This is a distinct advantage, since no modification need be made in the Group III procedure for the presence of phosphate.

[3] Since there is a definite limit to the amount of lead which can occur in Group II after the precipitation of Group I, the filtrate from the HCl precipitation was used as the starting amount for this determination.

TEN COMMANDMENTS

For the Student in Analytical Chemistry

HARRY BATEY *Cornell College, Mount Vernon, Iowa*

1. Thou shalt not kill unless thou canst prove that he did spit in thy unknowns.
2. Thou shalt honor thy neighbor's olfactory sensibilities.
3. Thou shalt not pencil titrate.
4. Thou shalt not take the name of thy professor in vain.
5. Thou shalt not remain forever on the pans of thy balance.
6. Thou shalt keep thy desk spotless—that thy days may be long in this laboratory.
7. Thou shalt not commit adulteration—of reagents.
8. Thou shalt love thy storeroom man as thyself.
9. Thou shalt not covet thy neighbor's endpoints, nor his success, nor his clean equipment, nor anything that is thy neighbor's.
10. Two days shalt thou labor, sweat, and swear in the laboratory—the others are days set aside for thy professor's peace of mind—and for the conservation of thine own sanity.

A Suggested Revision of the Position of Thorium in the Fourth Period of the Periodic Table

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A NEW SERIES OF RARE EARTHS

SCRUTINY of the succession formed by the atomic numbers of the noble gases, and the analogous relation between corresponding elements of the second and third periods, and also the third and fourth periods of the Periodic Table, has led us to accept and develop the hypothesis of J. Perrin (*1*) on the existence in period 7 of a series of elements similar to the rare earths, whose position would correspond to that now occupied solely by actinium (*2*).

This belief is supported by the work of I. Curie and P. Savitch on the transuranium element $R_{3\text{-}5h}$ obtained by them by neutron bombardment of uranium (*3*). This element is characterized by properties similar to those of the rare earths, and by a close resemblance to actinium.

On the other hand, the properties of neptune (93^{239}), a radioelement of 2.3 days' period obtained by McMillan and Abelson by activating uranium with neutrons, have suggested to these investigators the probable existence of a second series of "rare earths" with which uranium and element 93^{239} would be associated (*4*).

G. Mayer has recently confirmed the possible existence of the second series of "rare earths" predicted by McMillan and Abelson, coming to the conclusion that this series would be found in the proximity of element $Z = 92$ (*5*).

These experiments come close to confirming the possible existence of a second series of "rare earths" in the last part of the Periodic Table, which, according to what we have indicated, would begin with actinium ($Z = 89$).

This hypothesis raises two questions: should the known elements that follow in the natural classification occupy the position of actinium? That is, should thorium, protoactinium, and uranium be transferred to this position? Or what appears less probable, is it necessary to increase by fourteen units the atomic numbers of the above elements, in order to maintain their usual position? In this regard, we have verified the fact that the atomic numbers and X-ray spectra of these elements comply with Moseley's law.

The considerations to be detailed tend to justify moving thorium into the position occupied by actinium, which would represent a modification of Groups III and IV of the Periodic Table.

CHEMICAL ANALOGIES BETWEEN THORIUM AND THE RARE EARTHS

The close similarity of thorium to the rare earths is also manifested in nature, where the only mineral used for the industrial production of thorium compounds is monazite sand, which is largely composed of complex phosphates of thorium and the rare earths (*6*).

In other words, the primary source material for thorium compounds is the same as that used preferentially for obtaining the rare earths.

In addition, the most important of the chemical characteristics of the rare earths is their precipitability by oxalic acid from acid solutions, by which method the group can be separated easily from other substances. But this property is possessed also by thorium, whose oxalate is less soluble than the oxalates of the rare earths in strongly acid media, a property which is utilized in the analysis of that element (*7*).

At first glance, the tetravalency of thorium, which justifies its position in subgroup (A) of Group IV, would present difficulties in transferring this element to subgroup (A) of Group III, composed of trivalent elements such as scandium, yttrium, and the rare earths; nevertheless, it is important to note that the element which occupies the second place in the rare earth series and which would be the homolog of thorium in the actinium series is cerium, which is characterized by being tri- and tetravalent.

The oxide of thorium (ThO_2) has the same empirical formula as cerium oxide (CeO_2), the only stable anhydrous oxide of cerium (*8*); besides, cerium compounds in general have the same empirical formulas as the corresponding thorium compounds.

The oxides of thorium and cerium are characterized by being basic, while the oxides of titanium and zirconium, elements in the thorium subgroup, behave like acid anhydrides (*8*).

Salts of thorium, like those of cerium, have the property of forming numerous addition compounds; thus, for example, there are several series of derivatives of cerium nitrate homologous to the corresponding derivatives of thorium nitrate. Among these are found:

$$Ce(NO_3)_4 \cdot 2M'NO_3 \quad \text{and} \quad Th(NO_3)_4 \cdot 2M'NO_3$$

in which the radical M′ corresponds to monovalent radicals: NH_4, K, Na, Rb, ...

$$Ce(NO_3)_4 \cdot M''(NO_3)_4 \cdot 8H_2O \quad \text{and} \quad Th(NO_3)_4 \cdot M''(NO_3)_4 \cdot 8H_2O$$

in which the radical M″ corresponds to the bivalent radicals: Mg, Zn, Ni, Co, and Mn.

Also, the chlorides of cerium and thorium form with certain organic bases a series of homologous compounds such as the following:

$$CeCl_4 \cdot 2(C_5H_5N \cdot HCl) \quad \text{and} \quad ThCl_4 \cdot 2(C_5H_5N \cdot HCl)$$

$$CeCl_4 \cdot 2(C_9H_7N \cdot HCl) \quad \text{and} \quad ThCl_4 \cdot 2(C_9H_7N \cdot HCl)$$

Thorium, like the rare earths, combines with hydrogen and nitrogen, forming the corresponding hydride (ThH_4) and nitride (Th_3N_4); in contrast, titanium forms only adsorption compounds with those gases (*8*).

The chemical analogies existing between thorium and the rare earths and especially between thorium and cerium, similar although not as marked as those shown between actinium and lanthanum, would justify transferring thorium to subgroup (A) of Group III of the Periodic Table, in which the analogies are much better than those that can be established between thorium and the elements which actually do adjoin it in subgroup (A) of Group IV.

PHYSICAL ANALOGIES BETWEEN THORIUM AND THE RARE EARTHS

The crystal structure of thorium is that of a face-centered cube, similar to that of lanthanum, cerium α, and presumably similar to that of scandium and yttrium of subgroup (A) of Group III; in contrast titanium, zirconium, and hafnium which form with thorium subgroup (A) of Group IV have a hexagonal crystal structure.

Thorium carbide (ThC_2) crystallizes according to the tetragonal system, the same as the carbides of lanthanum (LaC_2), praseodymium (PrC_2), and neodymium (NdC_2), while the carbide of titanium (TiC) crystallizes in the cubic system the same as the carbide of zirconium (ZrC).

Furthermore, the oxide of thorium (ThO_2) crystallizes in the cubic system; cerium oxide (CeO_2) and praseodymium oxide (PrO_2) crystallize in the same way, while the oxide of titanium (TiO_2) crystallizes in the orthorhombic or tetragonal systems and the oxide of zirconium (ZrO_2) in the monoclinic, tetragonal, hexagonal, or cubic systems (*9*).

The isomorphism between cerium and thorium has been placed in evidence by the preparation of mixed crystals of thorium and cerium sulfates $ThCe(SO_4)_2 \cdot 4H_2O$; similarly the double nitrates of cerium, thorium, and ammonium $(Ce, Th)(NH_4)_2(NO_3)_6$. This isomerism has been further confirmed by the X-ray analysis of the oxides CeO_2 and ThO_2 (*10*).

ABNORMAL RELATION BETWEEN THE ATOMIC MASSES OF THORIUM, PROTOACTINIUM, AND URANIUM AND THOSE OF THE ELEMENTS WHICH COMPOSE WITH THEM GROUPS IV, V, AND VI OF THE PERIODIC TABLE

If one compares the values for atomic masses within a given group of the Periodic Table, a general rule will be observed: *The atomic mass of an intermediate element is less than the average for the atomic masses of the neighboring elements.* Thus, for example,

$$A_{Cl} = 35.457 < \frac{A_F + A_{Br}}{2} = \frac{19.00 + 79.916}{2} = 49.458$$

$$A_{Ba} = 137.36 < \frac{A_{Sr} + A_{Ra}}{2} = \frac{87.63 + 226.05}{2} = 156.84$$

$$A_{Zr} = 91.22 < \frac{A_{Ti} + A_{Hf}}{2} = \frac{47.90 + 178.6}{2} = 113.25$$

The only exceptions to this rule are presented by the atomic masses of hafnium, tantalum, and tungsten:

$$A_{Hf} = 178.6 > \frac{A_{Zr} + A_{Th}}{2} = \frac{91.22 + 232.12}{2} = 161.67$$

$$A_{Ta} = 180.88 > \frac{A_{Cb} + A_{Pa}}{2} = \frac{92.91 + 231}{2} = 161.955$$

$$A_W = 183.92 > \frac{A_{Mo} + A_U}{2} = \frac{95.95 + 238.07}{2} = 167.01$$

These three exceptions to so general a rule must be ascribed to the incorrect positions of thorium, protoactinium, and uranium in subgroups (A) of Groups IV, V, and VI.

It is interesting to note that if one accepts the value 229 for the atomic mass of actinium, the atomic mass of lanthanum agrees with the rule previously enunciated:

$$A_{La} = 138.92 < \frac{A_Y + A_{Ac}}{2} = \frac{88.92 + 229}{2} = 158.96$$

which confirms the correct position of the last-cited radioelement.

CONCLUSIONS

The hypothesis of the existence of a second series of rare earths in the position of actinium ($Z = 89$) raises the question whether the place now occupied by actinium should be filled by the elements which follow it in the Periodic Table, or whether their respective atomic numbers should be increased by 14 units.

As for thorium, study of its chemical and physical properties justifies its transfer to the position occupied by actinium. In its new position thorium would be found in subgroup (A) of Group III, composed of elements whose similarity to it is greater than that found by those forming subgroup (A) of Group IV, in which thorium is placed at present.

Furthermore, a comparative study of the atomic masses of the elements grouped with thorium, protoactinium, and uranium would render manifest the incorrect position of the elements mentioned and would suggest their transfer to the position occupied by actinium.

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An Application of the Polarizing Microscope to Reaction Study

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THIS paper describes a simple experiment in the qualitative study of reactions by means of the polarizing microscope. The reactions discussed are electrolytic, but the method is applicable to other types of reaction as well. The indispensable requirement is that materials and products shall differ in their effect upon polarized light.

This method offers an easy means for illustrating the progress of some reactions which would otherwise require a difficult and tedious procedure. It possesses value in teaching something of the use of the microscope, the physics of light, crystallography, electrolytic cells, and the chemistry of the reactions involved. It may be used as a stimulus to student investigation in applying the method to other reactions. A projecting microscope would make the process visible to an entire class at once.

THEORY

Crystals belonging to the isometric system are optically isotropic, that is, they possess the same refractive index in all directions. All other crystals are birefringent, at least in some directions (*1*). Between a "crossed" polarizer and analyzer an anisotropic crystal will be brilliantly lighted against a dark field, showing that it has broken the light from the polarizer into two components which will pass the analyzer. This effect will not be evident if the crystal happens to lie in a "position of extinction" or if the observer is looking down the unique axis of a tetragonal or hexagonal crystal. However, the double refraction of anisotropic materials is seldom overlooked because of such an orientation (*2*). There is little danger of oversight if the field includes a number of crystals.

First-year chemistry students are familiar with the electrolysis of the alkali metal chlorides according to the equation:

$$2KCl + 2H_2O \xrightarrow{\epsilon} 2KOH + H_2\uparrow + Cl_2\uparrow$$

It is not so well known that chlorine reacts with hydroxyl ion to form hypochlorite, chloride, and water. Then, with the aid of heat, the hypochlorite oxidizes itself still further to the chlorate:

$$3KClO \rightarrow 2KCl + KClO_3$$

The alkali metal bromides behave similarly.

It happens that potassium chloride and potassium bromide both crystallize in the isometric system, whereas potassium chlorate and bromate do not. It should be easy, therefore, to determine by means of polarized light whether any chlorate or bromate is being formed.

APPARATUS

We used an inexpensive microscope of 100–200–300 power purchased several years ago for twenty dollars. A polarizer-analyzer was purchased at the same time for eight dollars. Upon the polarizer is mounted an improvised revolving stage. The analyzer is in a cap which is set loosely on the eyepiece and rotated at will.

The electrolysis was carried out in a vial which was cut off to approximately one-ml. capacity. This vessel was mounted on the vertical spindle of a spring motor which turned at about eighty R.P.M. Stirring was found not essential in such a small cell, but it gave better yields. Two platinum wires were used as stationary electrodes. The circuit was arranged as in Figure 1,

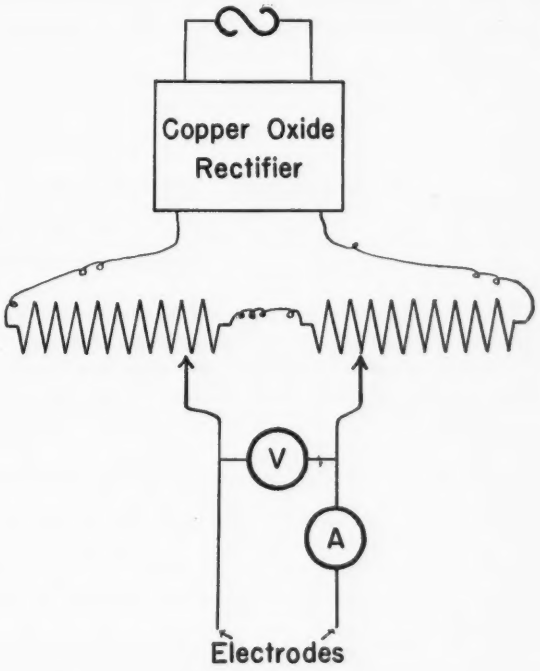

FIGURE 1

allowing the potential across the electrodes to be varied gradually from 0 to 5 volts. A storage battery or four dry cells in series with a variable resistor would provide a satisfactory current, instead of the rectifier.

METHOD

A saturated solution of the salt was placed in the vessel and a drop removed to a slide with a stirring rod. It was noted each time that the crystals at the beginning of the experiment were entirely isotropic. The vessel was held several minutes in a water bath just under 100°C. and then transferred to the stirrer and electrolyzed. After fifteen minutes a drop was removed for examination, the solution was reheated for a moment, and electrolysis continued.

Prior to each microscopic examination the solution was made slightly acid to remove the possibility of hydroxide, carbonate, or bicarbonate among the products. Hydrochloric acid was used for the chloride and hydrobromic for the bromide. The indicator was a drop of bromthymol blue mixed with a drop of the solution on a spot plate. Litmus paper may be used for the purpose, although the bleaching effect is rapid.

RESULTS

Certain rough quantitative estimates may be made of the results obtained as shown below. It will interest students to try the effect of varying the potential, the time, or the concentration of the salt. Favorable and unfavorable temperatures might also be determined.

Table 1 gives some data collected. Drops from 0.5 *M* solutions of potassium chloride and potassium chlorate were mixed in appropriate proportions on a slide to serve as rough standards of comparison for the "results" column. It might be pointed out that a potential of 2 volts, which was too low to discharge sufficient chloride ion for our purpose, produced an observable amount of bromate. For demonstration purposes saturated solutions, heat, 3.5 volts, and thirty minutes' time are recommended.

TABLE 1

Salt	*Temperature*	*Time in Minutes*	*Voltage*	*Results*
KCl	Room	20	3.5 ± 0.1	0
KCl	Hot	20	3.5 ± 0.1	20–25% $KClO_3$
KCl	Hot	30	2.0 ± 0.1	0
KCl	Hot	30	3.5 ± 0.1	33% $KClO_3$
KBr	Hot	30	2.0 ± 0.1	Slight
KBr	Hot	30	3.2 ± 0.1	Satisfactory for demonstration

It may be well to add here that the potassium chlorate produced in one run was positively identified by the immersion method (*3*). As mentioned, hydroxide, carbonate, and bicarbonate are destroyed before examination. There is one other possible anisotropic product of chloride, perchlorate, but F. Winteler has shown that no perchlorate is formed until nearly all the chloride is converted to chlorate (*4*).

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SALICYLAMIDE. THE AMMONOLYSIS OF METHYL SALICYLATE

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THE present difficulty of replacing laboratory stocks of acetic acid and its derivatives causes an instructor to hesitate to use the customary preparation of acetamide from ethyl acetate to illustrate the ammonolysis of esters. In this laboratory the ammonolysis of methyl salicylate

$$o\text{-}HOC_6H_4COOCH_3 + NH_3 = o\text{-}HOC_6H_4CONH_2 + CH_3OH$$

has proved to be a very satisfactory and economical substitute for the ammonolysis of ethyl acetate. The preparation involves little of the student's time and need not displace another preparation from the laboratory schedule.

Two milliliters (2.3 g.) of methyl salicylate and 20 ml. of concentrated ammonium hydroxide (28 per cent NH_3) are placed in a 50-ml. tincture bottle, stoppered *tightly*, and shaken thoroughly. The ester may be made to remain dispersed longer by the addition of 0.1 g. of a wetting agent such as Orvus, Dreft, Gardinol, etc., but this is not necessary. The mixture is set aside for a week. During this time the ester phase disappears. The clear solution is transferred to a beaker and diluted with 50 ml. of water which has been used to rinse the reaction bottle. The diluted solution is neutralized with hydrochloric acid. The liberated amide precipitates as the solution cools. The precipitate is collected on a suction filter and washed with 50 ml. of cold water (used in small portions) and dried. Without further treatment the product melts at 136–7°C. and the yields are good—about 70 per cent.

If suitable equipment, such as a ball mill frame, is available so that the reaction bottle can be turned end-over-end thirty to fifty times a minute the reaction is complete in less than eighteen hours and a 70 per cent yield is obtained in three hours.

This reaction is interesting in that esters of aromatic acids do not ordinarily ammonolyze readily at room temperature. The susceptibility of methyl salicylate to ammonolysis is doubtless due to the solubility imparted to both the ester and amide by the phenolic hydroxy group in the ortho position and should not be taken by the student to indicate that textbooks are incorrect in the statement that esters of aromatic acids ammonolyze with difficulty.

The Detection of the Mercuric Ion in Semimicro Qualitative Analysis[1,2]

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A NEW method for the detection of the mercuric ion in systematic semimicro analysis, involving the direct solution of mercuric sulfide in concentrated hydriodic acid and the final use of cuprous iodide for the detection of small amounts of mercury through a modification of Artmann's test (*1*), has been investigated. A study has also been made of the comparative efficiency of various reagents used in the standard procedures for the separation of the hydrogen sulfide group into subgroups, with particular reference to the separation of mercury. The efficacy of these separations is obviously of much greater importance in semimicro analysis than in the older macro schemes.

THE HYDRIODIC ACID TEST FOR MERCURY

The action of concentrated hydriodic acid on mercuric sulfide was applied by Caley and Burford (*2*) to the accurate separation of mercuric sulfide from its usual contaminant, sulfur, in the gravimetric determination of mercury.

$$HgS + 4HI \longrightarrow H_2HgI_4 + H_2S$$

If the resulting iodo-mercuric acid is diluted with water, a scarlet precipitate of mercuric iodide is produced. The formation of this precipitate was used as a qualitative test for mercury in microanalysis by Behrens (*3*), and Artmann (*1*) showed that the sensitivity of the test could be greatly increased by the addition of freshly precipitated cuprous iodide, which leads to the final formation of cupro-mercuric iodide (Cu_2HgI_4). However, in both of these cases the test is obtained by adding an iodide to a solution of a mercuric salt. The application of the direct action of concentrated hydriodic acid was therefore extensively investigated.

For all of the cation test solutions except mercury, 0.1 molar solutions were used in the earlier work. For most of the experiments, however, the solutions contained approximately 2 mg. of cation per drop. All volumes of mercuric chloride solution were delivered from calibrated pipets. Blank tests on solutions not containing mercuric ion were used in every investigation of the sensitivity of the separations and of the confirmatory tests. The hydriodic acid employed was the ordinary commercial 57 per cent stabilized by the addition of one to two per cent by volume of 50 per cent hypophosphorous acid, since the impurities present in such acid do not interfere, whereas much free iodine, as in the pure acid, is likely to obscure the results. Commercial cuprous iodide was found to be fully as sensitive as that freshly precipitated.

Preliminary experiments showed that simple dilution of the iodo-mercuric acid to produce the mercuric iodide was not sufficiently sensitive, but the following procedure was found to give excellent and consistent results:

Treat the well-washed mercuric sulfide precipitate in the centrifuge tube with 1 to 5 drops (depending on the amount of precipitate) of concentrated hydriodic acid, and heat to 100° for one minute. If a residue remains, dilute the solution to one ml. and filter into a small porcelain crucible. Otherwise transfer the solution directly to the crucible. Evaporate *just to dryness on a steam or water bath.* Add one drop of 3 *N* nitric acid and again evaporate just to dryness. The formation of a pink to scarlet deposit of mercuric iodide indicates the presence of mercury. If no precipitate appears, still smaller amounts may be detected by adding one ml. of distilled water, heating on the steam bath, and then adding a pinch (1 to 2 mg.) of solid cuprous iodide. The solution is again evaporated just to dryness. The formation of a pink to dark red deposit of cupro-mercuric iodide indicates the presence of mercury.

Note 1.—The solution should not be evaporated beyond dryness because of the volatility of mercury salts. This is particularly true when nitric acid is present.

Note 2.—The nitric acid is added to remove any iodine and to counteract any reduction of mercury by hypophosphorous acid. It must be evaporated before adding cuprous iodide, since otherwise oxidation of the latter compound may take place.

The interference of the other hydrogen sulfide group ions with the final test for mercury was tested on 0.25 mg. mercuric ion samples by adding 3 drops of 0.1 molar solutions of each of the other ions to separate samples after treatment of the mercuric sulfide with hydriodic acid. It was found that lead, copper, cadmium, and tin ions do not interfere with the appearance of the red mercuric iodide after the treatment with dilute nitric acid. In view of results previously obtained (*4*) it is somewhat surprising that tin does not interfere by forming red stannic iodide. Probably the nitric acid evaporation changes any stannic iodide to the white oxide. When arsenic and antimony were present good tests were not always obtained until cuprous iodide was added. As Artmann (*1*) observed, bismuth ion in high concentration obscured the test.

The mercuric iodide test, with its characteristically colored product, is about two to three times as sensitive as the usual stannous chloride test in student hands, while that with cuprous iodide is twenty to thirty times as sensitive. The iodide test also avoids the necessity of boiling out excess chlorine from the aqua regia, with

[1] Presented before the Division of Chemical Education at the 102nd meeting of the A. C. S., Atlantic City, New Jersey, September 9, 1941.

[2] Abstract of the thesis submitted by A. F. Wichrowski to the Faculty of Wesleyan University in partial fulfilment of the requirements for the degree of Master of Arts, 1940.

[3] Present address: Chase Brass Company, Waterbury, Connecticut.

consequent loss of mercury. The comparatively high cost of hydriodic acid should not be a deterrent, since only a very small quantity is used. The sensitivity of all of the three methods of detecting mercury mentioned above may be increased by the use of special micro technic. Artmann claims that the use of cuprous iodide will permit the detection of 0.00006 mg. of mercuric ion either on microscope slides or on spot paper. No such sensitivity would be expected in ordinary systematic analysis.

In determining the sensitivity of the proposed method, the mercuric ion was detected in the presence of other ions when mixtures were subjected to ordinary microanalysis. Hence, the efficiency of various methods of separating the hydrogen sulfide group into its subgroups, particularly as far as mercury is concerned, and also the final usefulness of this test as a routine analytical method, were both determined.

AMMONIUM POLYSULFIDE AS A SEPARATING AGENT

Ammonium polysulfide, though often used to separate the copper subgroup from that of tin, is not very satisfactory (*5*, *6*). The polysulfide dissolves a considerable quantity of copper sulfide, especially when arsenic, antimony, and tin are present. In the presence of cadmium and tin, much of the latter remains in the copper subgroup. The presence of copper in the tin subgroup was noted in this study, but was not investigated critically. The amount of copper dissolved did, however, seem fairly small. Most important of all, from the point of view of this investigation, the polysulfide also dissolves some mercuric sulfide.

In the first series of experiments, samples containing varying amounts of mercury, but no other hydrogen sulfide group cations in a total volume of 3 ml., were analyzed by the systematic procedure to compare the sensitivity of the mercuric iodide and classical stannous chloride methods. It was found that 0.05 mg. of mercuric ion would give the iodide test without the addition of cuprous iodide, but 0.12 mg. was required to give a reasonable stannous chloride test. The analysis was then extended to include mixtures of the mercuric ion and the other ions of the hydrogen sulfide group. More than fifty different analyses were carried out with from 5 to 15 milligrams of each ion. Fresenius (*7*) reported that when mercury and tin are present together, some of the tin remains in the copper subgroup and some of the mercury goes into the tin subgroup. Fifteen analyses of varying mixtures showed that this is true also in semimicro analysis, and tin was found in the copper subgroup whether or not cadmium was present. In many cases a better test for tin was obtained in the copper subgroup than in the tin subgroup. Repeated treatments of the group sulfide precipitate with ammonium polysulfide had no appreciable effect.

It does not seem to have been previously reported that arsenic and antimony ions also favor the solution of mercuric sulfide in the polysulfide reagent. The arsenic and antimony do not, apparently, appear in the copper subgroup, but some mercuric sulfide does dissolve into the tin subgroup. Comparative experiments showed that each of these ions is about as effective as tin in increasing the solubility of the mercuric sulfide. For example, 0.25 mg. of mercuric ion gave a test for mercury in the copper subgroup only after the addition of cuprous iodide when 12 to 15 mg. of arsenic, antimony, or tin, and no other ions were present in the original mixtures. This would indicate that about four-fifths of the sulfide had dissolved. Good tests for mercury could also be obtained in the tin subgroup. This effect was less noticeable if copper, cadmium, or bismuth were also present, but lead seemed to have no effect. Mixtures containing all three of the tin subgroup ions gave uncertain tests for 0.5 mg. even when other copper subgroup ions were present. To summarize our results, 0.25 mg. of mercuric ion can be detected in the presence of 15 mg. lead, 15 mg. bismuth, 10 mg. copper, 12 mg. cadmium, and 12 mg. of any single ion of the tin subgroup if cuprous iodide is used for the final detection. The safe limit when all the tin group ions are present is about one mg., and with this amount of mercury the test is positive without the addition of cuprous iodide.

Ammonium sulfide as a separating agent was not extensively investigated. However, a few analyses showed that the presence of the tin subgroup ions also had an influence on the solubility of mercuric sulfide in this reagent, and tin also appeared in the copper subgroup. If the monosulfide is used, tin must be oxidized to the stannic condition. The alkali sulfides and polysulfides were not investigated, since it is claimed that bismuth and copper sulfides are somewhat soluble in them (*8*, *9*). A few tests were run on the reagent recommended by Welsh and Weber (*10*) which consists of ammonium polysulfide and 5 per cent sodium hydroxide, but mercuric sulfide is partially soluble in this reagent, also.

SODIUM HYDROXIDE-AMMONIUM CHLORIDE AS A SEPARATING AGENT

This reagent is known to dissolve some mercuric sulfide (*11*, *12*). To counteract this the mercuric sulfide is reprecipitated by the addition of ammonium chloride and tested for in the copper subgroup (*13*), or separations are carried out in both groups (*14*).

Walker (*15*) and Curtman and Marcus (*11*) mention that the presence of tin subgroup ions influences the solubility of mercuric sulfide in alkali hydroxides, but give no data. Rough comparison experiments with mixtures containing 4 mg. of mercuric ion and 8 mg. of each of the ions of the tin subgroup showed that on treatment with 2 *N* sodium hydroxide, with arsenic all, with tin about one-half, and with antimony about one-third of the mercuric sulfide dissolved. The well-washed mercuric sulfide proved essentially insoluble when tested by itself. Most of the dissolved mercuric sulfide is reprecipitated when ammonium chloride is added to the oxy-sulfo complexes, and if the solution is centrifuged *and* filtered, the quantity of mercury passing into the tin subgroup is not sufficient to interfere with the

rhodamine B test for antimony. However, a test for mercury could always be obtained in the tin subgroup, even when but very small quantities of mercury were initially present. It should be mentioned also that the presence of copper subgroup ions does not seem to inhibit the influence of the tin subgroup sulfides on the solubility of mercuric sulfide.

When sodium hydroxide is used as a separating agent, stannous ion must be oxidized to stannic, since stannous sulfide is not very soluble in sodium hydroxide. Considerable trouble has also been experienced in this laboratory because of the failure of stannic sulfide to dissolve rapidly enough. Potassium hydroxide is apparently somewhat more efficient in dissolving either of the tin sulfides (*11*). If the divalent tin is oxidized by evaporation with nitric acid there is considerable danger of loss of mercury by volatilization (*16*). Our experiments showed that as much as 0.5 mg. of mercuric ion in one or two ml. could be completely volatilized on evaporation with two drops of concentrated nitric acid. With the dilute acid used to remove excess iodine in the test, the loss is much less, and when one mg. of mercuric ion was present in the test samples, a test for mercury could be obtained even when the crucibles had been heated on the steam bath for 15 minutes after coming to dryness.

Approximately 70 samples of "unknowns" of varying composition were investigated by systematic analysis using the sodium hydroxide-ammonium chloride separating agent. In mixtures containing more than 2 mg. of mercury small amounts of antimony and tin remained in the copper subgroup after the supposed separation with sodium hydroxide. Heating the solution after the addition of ammonium chloride did not prevent this. In the absence of mercury, separations could be obtained, although the tin apparently dissolves slowly. This effect of mercuric ion on antimony and tin does not seem to have been reported previously.

When the nitric acid evaporation method for oxidizing stannous ion was used it was found that 0.5 mg. of mercuric ion could be detected in the presence of 4 mg. of each of the other ions of the hydrogen sulfide group. A test for mercury could also be obtained in the tin subgroup with these samples. When the nitric acid evaporation was omitted the reaction was sensitive to 0.12 mg. of mercuric ion in 4 mg. of any of the other ions or of any combination. However, this method endangers the detection of any stannous tin originally present, and, again, tests for mercury can be obtained in the tin subgroup.

SODIUM HYDROSULFIDE AS A SEPARATING AGENT

The sodium hydrosulfide reagent originally proposed by Sneed (*6*) was unsatisfactory because it dissolved considerable bismuth sulfide and dissolved stannous sulfide only with difficulty. Consequently, the reagent recently proposed by Maynard, Barber, and Sneed (*17*) is now made up so that each liter of 3 *N* sodium hydroxide saturated with hydrogen sulfide contains 4 g. of sulfur and 3.5 g. of added sodium hydroxide. It is thus essentially sodium hydrosulfide with added sulfur to oxidize the tin.

With such a reagent mercuric sulfide is dissolved into the tin subgroup as a sulfo-complex, and the separation of mercury from arsenic, antimony, and tin is therefore necessary. This is usually done by treating the reprecipitated sulfides with 12 *N* hydrochloric acid, in which case the antimony and tin dissolve but the arsenic and mercuric sulfides are not supposed to be appreciably soluble. Such a procedure is probably successful in macro analysis and has been applied to semimicro analysis. However, it was not deemed advisable in this investigation because, contrary to popular opinion, mercuric sulfide, even when aged, is appreciably soluble in hot concentrated hydrochloric acid (*18*). Moreover, it was found possible to apply the hydriodic acid technic directly to the mixture of tin subgroup sulfides containing mercuric sulfide.

Preliminary experiments showed that 5 drops of concentrated hydriodic acid were necessary to dissolve 4 to 5 mg. of mercuric ion freshly precipitated as mercuric sulfide, and hold it in solution when the solution is diluted to one to 1.5 ml. and saturated with hydrogen sulfide. When 4-mg. solutions of the other tin subgroup ions were subjected to this procedure none of the arsenic sulfide appeared to dissolve; the antimony sulfide and also the stannic sulfide dissolved in the acid but reprecipitated on saturation with hydrogen sulfide. A very small quantity of tin may not reprecipitate, but this was not a sufficiently large amount to give a qualitative test in the usual manner. The 5 drops of concentrated acid are sufficient to keep all the mercuric sulfide in solution in the presence of any combination of 15 mg. of the tin subgroup ions. The following procedure is therefore recommended after the hydrogen sulfide group has been divided by treatment with two 0.6-ml. portions of the sodium hydrosulfide reagent at 90°.

> Reprecipitate the sulfides of the tin subgroup with dilute hydrochloric acid and wash thoroughly. Treat the precipitate in the centrifuge tube with 5 drops of concentrated hydriodic acid, dilute to one to 1.5 ml. with distilled water, heat to 100°, and saturate with hydrogen sulfide for one minute, cool, centrifuge, and filter. The remainder of the analysis is conducted as directed previously, and the analysis for the other group elements may be conducted in any suitable manner. It is important that these other sulfides be washed free from hydriodic acid, however, since this is likely to interfere with subsequent tests.

Test analyses showed that in general the Sneed reagent is the most satisfactory of those investigated for the separation of mercury. When from 0.5 to 4 mg. of mercuric ion were present along with 4 mg. of each of the other ions of the hydrogen sulfide group, good tests for mercury as mercuric iodide were obtained after the evaporation with one drop of 3 *N* nitric acid. When the more sensitive cuprous iodide test was used 24 analyses showed that 0.05 mg. of mercuric ion could be easily detected in 4 mg. of each of the other ions. The mercury test was equally sensitive in the presence of 4 mg. of the ions of lead, copper, bismuth, and cadmium and the complete absence of arsenic, antimony, and tin. In addition, no test for bismuth ion could be obtained

in the tin subgroup. In all the analyses no nitric acid evaporation was necessary to oxidize stannous tin before precipitation with hydrogen sulfide.

With larger amounts (2 to 4 mg.) of mercuric ion present, however, it was found that the separation of mercuric sulfide from the copper subgroup by sodium hydrosulfide was incomplete. This is in agreement with the observations of Noyes (*19*), and Middleton and Willard (*20*). In addition a trace of mercury seemed to be retained in the sulfides of arsenic, antimony, and tin after the treatment with hydriodic acid. However, these incomplete separations did not seem to cause any interference. The mercuric sulfide that remained in the copper subgroup was separated from the other sulfides by dilute nitric acid, and the little mercuric sulfide that remained with the sulfides of arsenic, antimony, and tin did not interfere with the usual tests for these ions.

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THE LAWS OF DEFINITE COMPOSITION AND DEFINITE PROPORTIONS

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DEFINITE composition arises from two distinct causes: (1) in molecular compounds, from union of a definite number of atoms of each element in forming a molecule; (2) in ionic compounds, from the fact that oppositely charged ions must be present in definite proportions in order that the substance as a whole may be electrically neutral. The law fails with many of the silicates because an indefinite number of silicon atoms in the silicate network (a "giant anion") may be replaced even by atoms of a different valence from silicon. The consequent alteration in the charge on the anion is then compensated by an alteration in the kind (or, sometimes, in the number) of the cations incorporated into the crystal structure. The law also fails whenever an indefinite number of the atoms of a crystal (1) may be withdrawn, without causing the structure to collapse, (2) may be replaced by other atoms, or (3) may accommodate foreign atoms between them. Thus, three different types of solid solutions are produced, which have only a definite *limiting* composition, perhaps expressible by a definite formula.

When reactants and resultants are all of definite composition, it is commonly assumed that a given reaction, *unaccompanied by others*, will transform them in definite proportions by weight. The words in italics require explanation, since even so simple a reaction as the direct union of hydrogen and oxygen to form water involves several successive steps, and may proceed by several different mechanisms at once.

Let s different substances be concerned in a reaction. Then $s - 1$ definite ratios must be established between the weights (or numbers of molecules) of the reactants, if the law of definite proportions is to hold. We also have x independent equations, each stating that the total weight (or total number of atoms) of some element or group of elements remains constant. For a unique solution, the number of variables (weight ratios) to be determined must equal the number of independent equations, hence $s = x + 1$. In other words, the law holds, and the reaction may be represented by a balanced equation, whenever the number of substances appearing in the equation exceeds by one the number of independent elements or undecomposed radicals. Independent elements are those not brought into balance in the process of balancing with respect to other elements. In the decomposition of calcium carbonate into calcium oxide and carbon dioxide, there are only two independent elements, since oxygen is found to be in balance when the equation has been balanced with respect to calcium and carbon. In displacement or exchange reactions, only three of the four elements or radicals displaced or exchanged are independent.

By this test the law of definite proportions is found to hold for all of the simplest types of chemical reactions (direct union, decomposition, internal rearrangement, displacement, exchange) and for their combination in consecutive reactions, whenever the intermediate steps are completed. It fails when the simple reaction types occur simultaneously or when intermediate steps remain uncompleted.

Potential Energy Curves in General Chemistry

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QUANTUM mechanics, to most teachers of general chemistry, is a highly specialized science which has become the fashion of the day in the field of chemical physics. Unfortunately, too few chemistry teachers take advantage of this fashion in presenting some of the useful concepts of quantum mechanics in the elementary, general chemistry course. And yet potential energy curves, one of the devices of quantum mechanics, undoubtedly afford the teacher a vivid method for explaining to the beginning student the concept of energy relations among atoms. At the same time, the use of potential energy curves familiarizes the student with concepts which he will encounter in considerable detail later in his course in physical chemistry.

Let us consider the energies involved in an isolated system containing *two magnets*. If the magnets are brought closer together end-to-end the energy of the system will change in one of two ways. If like poles are facing they repel one another, and energy must be supplied to overcome the repelling forces as the two magnets are pushed closer together. If, on the other hand, unlike poles are brought together, the attractive force between them releases energy from the system.

The same relationships apply to an electrostatic force, such as is shown in Figure 1. Here *two electrons* (e + e) are forced together, the potential energy of the system being plotted against the distance apart of the electrons. Because there is repulsion, external forces must be applied as the electrons are pushed closer and

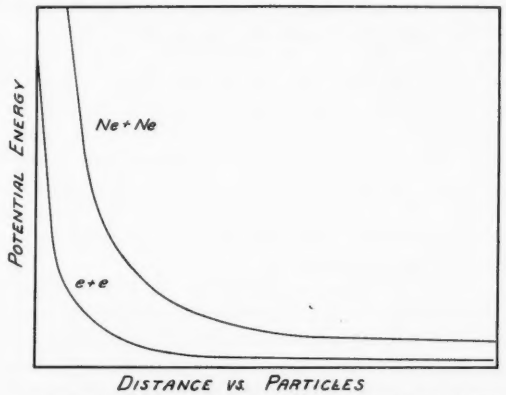

FIGURE 1.—FORCES INVOLVED IN BRINGING TWO ELECTRONS (e + e) OR TWO NEON ATOMS (Ne + Ne) TOGETHER

closer together. This force varies in accordance with the well-known inverse-square law, the potential energy of the system increasing as the electrons are forced together. The resultant potential energy of the system is shown in the figure.

Next let us consider the case of *two hydrogen atoms* being brought together. In this instance there is a

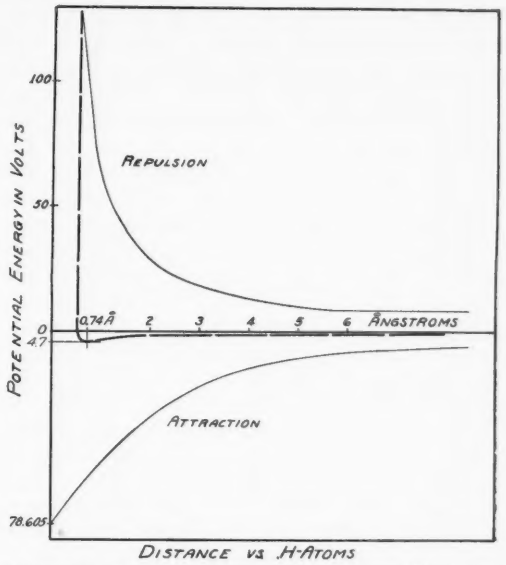

FIGURE 2.—POTENTIAL ENERGY CURVES FOR TWO HYDROGEN ATOMS

repulsive force between the planetary electron of each atom; also there is a repulsive force between the two positively charged nuclei. At this stage in our story, quantum mechanics enters. By means of this special mathematical technic it is possible to calculate the magnitude of these forces as the two hydrogen atoms are brought closer together. A decade ago the Morse curve equation, a mathematical expression to construct these potential energy curves, was employed. Today further specialized wave mechanics slightly improves these calculations. In substance, a calculation of the repulsive forces by such methods gives the upper curve shown in Figure 2.

There is also an *attraction* between the two hydrogen atoms, the interaction between the electron of one atom and the positively charged nucleus of the other atom. Again quantum mechanics, brought to bear upon the problem, can calculate the magnitude of the attraction. The curve for this attraction is the lower curve in Figure 2. The broken line curve shows the summation of the repulsive and attractive curves; it is the potential energy curve for two hydrogen atoms brought together. A portion of it is redrawn in Figure 3. It will be observed in Figure 3 that a minimum occurs at a point at which the two hydrogen atoms are 0.74 Angström units apart. The distance 0.74 A. is therefore

[1] Presented before the Division of Chemical Education at the 102nd meeting of the A. C. S., Atlantic City, New Jersey, September 9, 1941.

a critical distance in bringing two hydrogen atoms together. It is a distance calculated by quantum mechanics. It represents the diameter of a hydrogen molecule. The physical interpretation of this curve is that two hydrogen atoms form a stable configuration when 0.74 Angströms apart and cannot be separated unless energy is supplied to overcome the large attractive forces. In other words, quantum mechanics confirms for us that the *hydrogen molecule is diatomic.*

A similar calculation may be made for a system comprising *two neon atoms.* In this case the interactions of the various electrons and positive nuclei are decidedly more complicated than in the case of hydrogen. The number of terms involved is large indeed. But by laborious application of the wave mechanics the curve shown in Figure 1 for Ne + Ne can be constructed. Attraction and repulsion result in a composite curve not unlike that of the two-electron case. Unlike hydrogen, no deep valley exists at some critical distance. What valley there is is so slight that even room temperature supplies the energy necessary to separate the two neon atoms. Physically, this curve corroborates the observation that *neon is monatomic.*

Potential energy curves are especially advantageous in illustrating *energy relations during chemical reaction.* Again the quantum mechanics by which the curves are constructed must be left to the course in physical chemistry; but the curves themselves may be fruitfully employed in elementary general chemistry. In the case of a chemical reaction the potential energy is a function of all of the interaction forces of the different

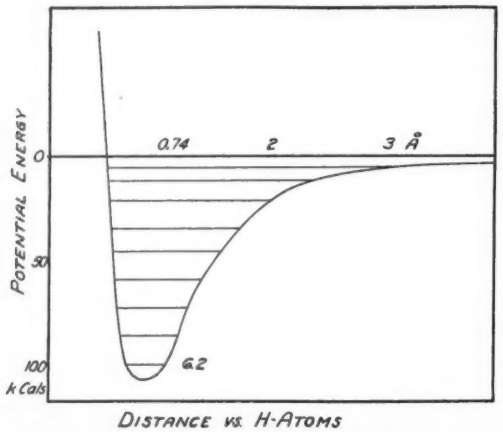

FIGURE 3.—POTENTIAL ENERGY CURVE FOR TWO HYDROGEN ATOMS, SHOWING THE COMPOSITE OF THE REPULSIVE AND ATTRACTIVE FORCES

atoms entering into the chemical reaction. In Figure 4 the potential energy[2] of the system before reaction is represented by point *A;* the potential energy of the system after reaction, by point *B.* This is, of course, a considerable simplification of the actual methods of quantum mechanics, in which potential energy *surfaces* are studied,[3] but the concept is valuable to the beginning student. In both curves in Figure 4 it is obvious that the reactants must be given some energy in order

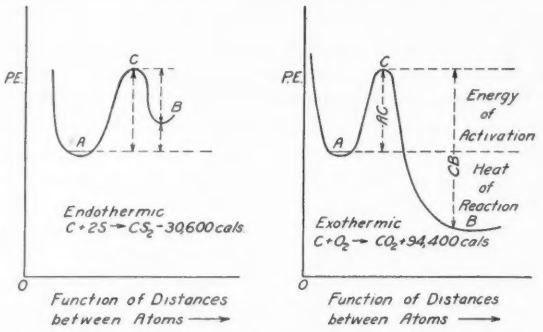

FIGURE 4.—POTENTIAL ENERGY CURVES FOR ENDOTHERMIC AND EXOTHERMIC REACTIONS

for reaction to occur, *i. e.,* in order to go from position *A* to position *B,* energy must first be supplied to the system to take it over the *potential energy hump.* The amount of this energy will be different for different reactions. It is called *energy of activation.*

Now the curves for the two reactions illustrated in the figure have one striking difference: *CB* for the formation of CO_2 is greater than *AC*; but *CB* for the formation of CS_2 is less than *AC.* The physical interpretation of this in the oxidation of carbon is that more energy is given off than is required to raise the system over the potential energy hump; the reaction is exothermic. For the combination of carbon and sulfur, on the other hand, the reaction is endothermic.

The magnitude of the difference $CB-AC$ is a measure of the exothermicity of the reaction. The thermite reaction, for instance, would show a much greater difference than the oxidation of carbon.

The use of these curves immediately answers for the student a troublesome question which frequently arises: Why does a lump of coal, which gives off heat when it burns, have to be heated in order to make it burn? The potential energy hump, which must be surmounted before reaction may occur, visualizes the answer. At the same time, these curves are not merely a teaching device: they are part of the science of research in wave mechanics.

Let us next focus our attention on the *height of the potential energy hump.* The higher the hump, the greater the energy of activation necessary for reaction to occur. Figure 5 shows three reactions which proceed measurably at different temperatures. The combination of phosphorus occurs rapidly at room temperature because little energy need be supplied to take it over the hump. The hydrogen-oxygen reaction, on the other hand, takes considerably more energy—a temperature of 550°C., or an electric spark. Note again that the height of the hump has little to do with the exothermicity of the reaction.

[2] The author is indebted to D. Van Nostrand Company, Inc., for permission to publish Figures 4 and 5 in this paper.

[3] EYRING AND WALTER, J. CHEM. EDUC., 18, 73 (1941).

Rate of reaction is a measure of the rate at which reactant molecules attain energies corresponding to heights C, C', C'', etc. In a mixture of molecules, only

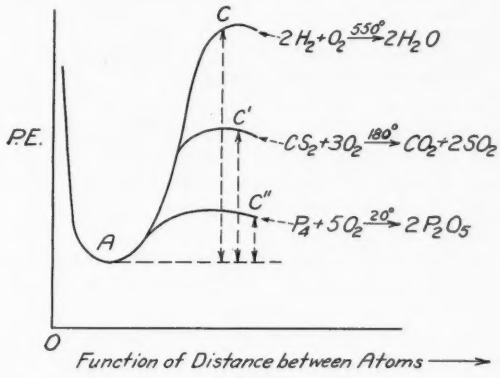

FIGURE 5.—ENERGY OF ACTIVATION FOR DIFFERENT REACTIONS

the most active ones have energies sufficient to take them over the hump. Like a flock of sheep escaping over a fence, the most active ones are the first to go, followed one by one as each sheep attains sufficient energy.

In Figure 6, for instance, only molecules with energies greater than C can react. This figure emphasizes how very few of the molecules in a system are available for reaction at any given instant. The shaded portions of the enlargement show how a ten-degree rise in temperature may double the number of reacting molecules (*e. g.*, double the area beyond C).

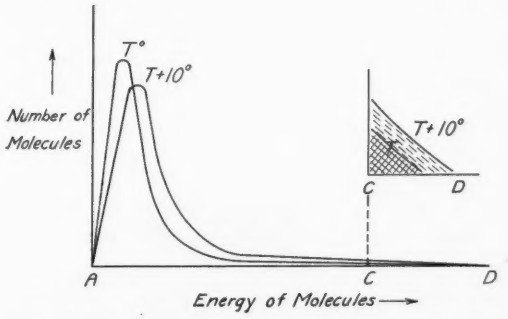

FIGURE 6.—MAXWELL-BOLTZMANN ENERGY-DISTRIBUTION CURVES. ONLY MOLECULES WITH ENERGIES GREATER THAN C REACT

Insert: Portion CD increased more than a billion fold to show that a ten-degree rise in temperature may double the area beyond C (*i. e.*, may double the number of reacting molecules).

Radioactive disintegration offers another instance of the application of quantum mechanics. From what has been said about rate of reaction, it might be surmised that radium A, which decays slowly relative to radium C′ (half-lives of 1590 years and 10^{-6} seconds, respectively) has a relatively higher hump. Actual calculations show that the humps are far too high to account for the rates of these radioactive disintegrations. This was a problem classical mechanics could not solve. But quantum mechanics explained it[4] as an effect related to the probability of the alpha particle passing spontaneously from position A (Figure 7) to position B, a so-called "tunnel effect." This explanation also accounted for the fact, unexplained for two decades by classical mechanics, that radioactive decay follows the laws of probability. Turning to Figure 7, the rate of transition from A to B, *i. e.*, the rate of radioactive decay is, according to the Gurney-Condon expression, exponentially dependent upon the area under the barriers, in the curves for the three radioactive substances. The relative heights of RaC′, RaA, and U above position B give the energies of the emitted particles. In comparison with the other two, RaC′

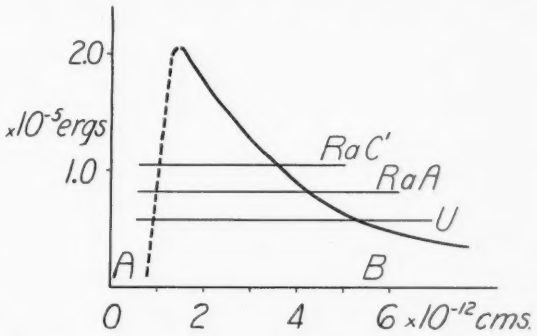

FIGURE 7.—POTENTIAL ENERGY CURVES FOR RADIOACTIVE DISINTEGRATIONS (*after Gurney and Condon*)

has (1) the greatest energy of the emitted particle, (2) the smallest area under the barrier, and therefore (3) the greatest rate of decay. Items (1) and (3), predicted in this way by quantum mechanics, simply confirm the Geiger-Nuttall relation which states that the rate of radioactive decay is greater, the greater the energy of the ejected particle. Thus RaC′, RaA, and U eject alpha particles with velocities 1.92, 1.69, and 1.4 ($\times 10^9$) cm. per second respectively, and have half-lives of 10^{-6} seconds, 3.05 minutes, and 4.4×10^9 years, respectively. Quantitatively, Gurney and Condon found that the potential energy curves for atoms belonging to the same radioactive series were essentially of the same form, differing only in the areas under the barrier. A calculation of these areas in accordance with items (2) and (3) actually predicted half-lives for these atoms.

Use of potential energy curves in beginning chemistry courses therefore offers a splendid introduction to the devices of quantum mechanics and, at the same time, enables the student to visualize the otherwise difficult concepts of energy change accompanying chemical reactions.

[4] GURNEY AND CONDON, *Nature*, **122**, 439 (1928); *Phys. Rev.*, **33**, 127 (1929). GAMOW, *Z. Physik.*, **51**, 204 (1928).

Leather

KENNETH E. BELL

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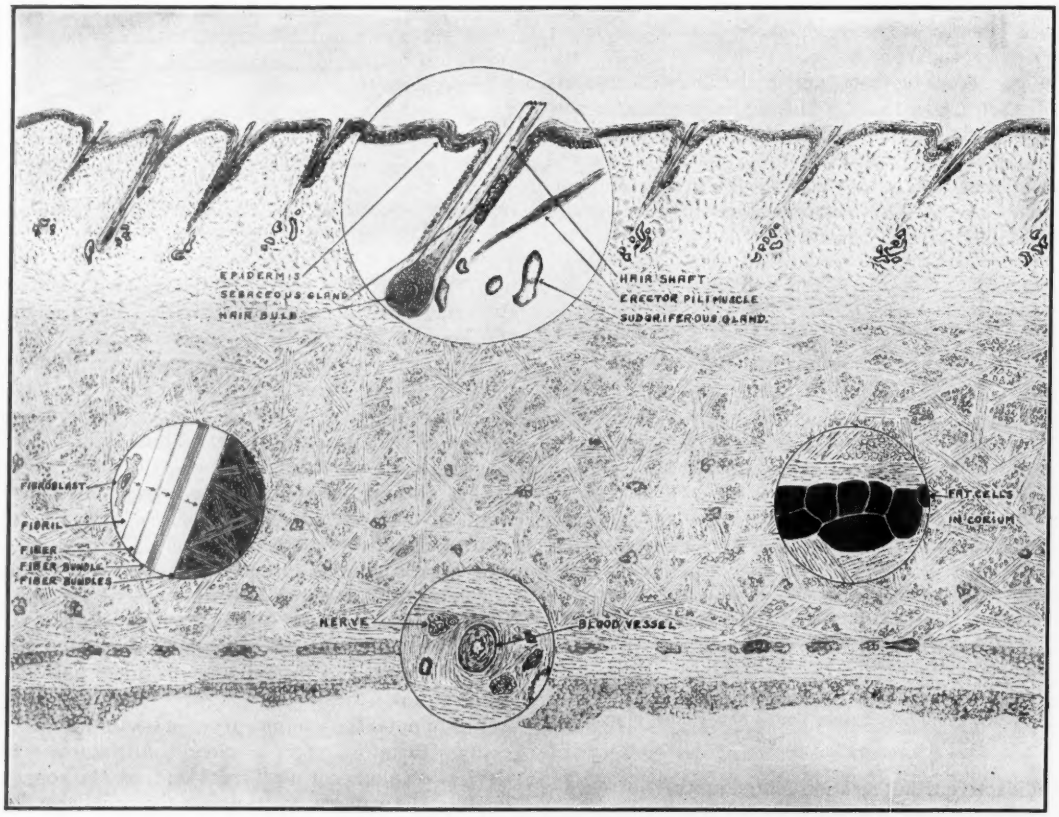
LEATHER has been called "the most historic of useful materials." The earliest written records tell of the use of leather for clothing, armor, and bedding. We read in the Bible: "Unto Adam and also unto his wife did the Lord God make clothes of skins and clothe them." The Hebrews, Greeks, Romans, and Moors employed leather extensively. Leather guilds were important in the Middle Ages and today leather is still one of the basic industries.[1] While for centuries tanning was a home industry, the small units with hand methods began to give way about a hundred years ago to large plants equipped with machinery. Today, tanning is operated as a big business, depending largely on packing houses for its raw material.

Leather is used largely in shoe making—both for uppers and soles; for coats and gloves; belting for machinery; and luggage. It is employed for aviators' clothing, in the construction of gasoline tanks for fighting planes, and in many other surprising places. Why has it continued in demand in these days of synthetic substitutes? We must study its wonderful structure for an answer. Figure 1 shows a magnified, diagrammatic view of the edge of a steer hide, after it has been cut through with a sharp knife.

[1] If you are interested in the history of leather through the ages send five cents to the Tanners' Council of America, 100 Gold Street, New York City, for a copy of "The Romance of Leather." This contains a great deal of interesting and instructive material.

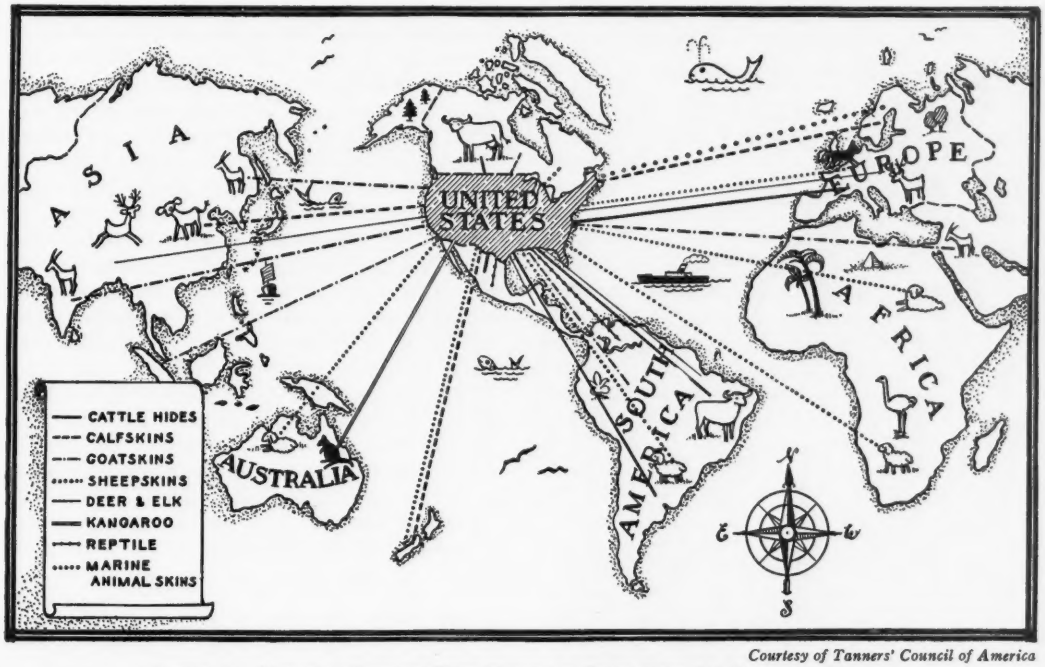


Courtesy of Tanners' Council of America

FIGURE 1.—DIAGRAMMATIC DRAWING OF A TYPICAL CROSS SECTION OF FRESH STEER HIDE
The whole section represents low magnification while the inserted circles represent structures under higher magnification to give more detail.

At the top we see the epidermis—the outer or hair side of the hide. The circle shows how the hair grows from a bulb located in a pocket in the epidermis. The sweat (sudoriferous) glands and the muscles that make hair stand on end (erector pili) are also illustrated.

The tanner must take hides and skins—a by-product of the packing industry—varying widely in size, shape, condition, and texture, and secure volume production of a uniform product. Formerly this was a closely guarded art; today's method, producing a more uniform product, utilizes chemistry as a guide and control.



Courtesy of Tanners' Council of America

FIGURE 2.—AMERICAN TANNERS USED HIDES AND SKINS FROM ALL OVER THE WORLD

On the live animal, the outer surface of the hide is dead; below this the grain composed of dense but living material extends to the bottom of the hair bulb in the circle. The grain imparts the characteristic appearance to leather, and has great resistance to wear or rubbing. The body of the hide, or corium, is represented by straight lines, or fiber bundles. These are intermixed in all directions, and when tanned into leather have the ability to withstand repeated flexing. No matter from what direction stresses come, some fibers are in a position to take them. So far, none of the synthetic leathers has reproduced this structure and so lacks its character.

Besides resistance to abrasion and flexing, leather *breathes*. That is, water vapor diffuses or passes through leather, permitting the escape of perspiration and heat. This explains why leather is comfortable when other materials are hot and unpleasant.

Cattle hides, calfskins, sheepskins, goat and kid skins are those most widely employed for tanning. Figure 2 shows the world-wide sources of many hides and skins. Before the restrictions on trade due to unsettled world conditions, chrome ore for tanning came from New Guinea, Africa, and Greece; chestnut oak bark from the United States; quebracho extract from South Argentine trees; sumac from Sicily; gambier from the Dutch East Indies; and so on through a long list.

The tanner must take hides and skins—a by-product of the packing industry—varying widely in size, shape, condition, and texture, and secure volume production of a uniform product. Formerly this was a closely guarded art; today's method, producing a more uniform product, utilizes chemistry as a guide and control.

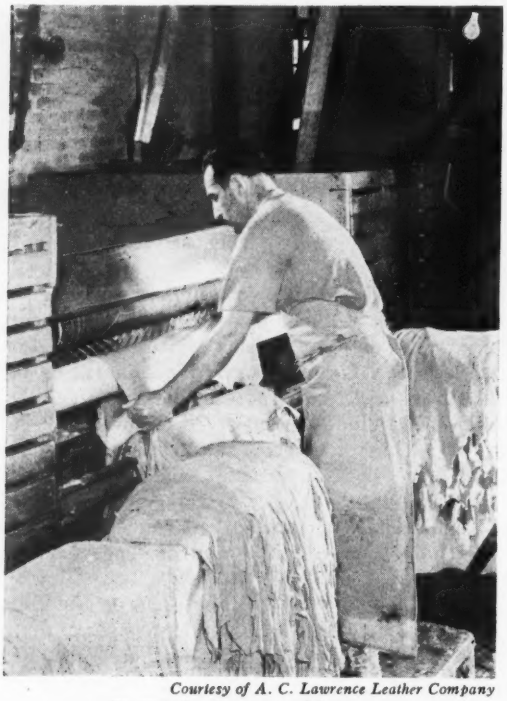
Hides and skins are colloidal, organic materials, composed mainly of various proteins. Their chemistry is very complex and not entirely mastered. It is known that these proteins are built up from amino acids, which act both as acids and bases. Excessive alkalinity or acidity swells hides greatly. If allowed to remain wet, or at high temperatures, hides will dissolve or decompose. The tanner must take into account or utilize these peculiarities when carrying out his task of making hides or skins into leather (which, by definition, is to render them insoluble and no longer subject to putrefaction).

He has the choice of finishing them on the grain or hair side to make so-called grain leather, or of finishing on the flesh side to make suede leather. If he desires to make upper leather, thinner hides or skins are used, or else he splits off some of the flesh side so that thickness and bulk will not be too great for today's conditions. If sole or heavy leather is desired, larger and heavier hides are tanned and methods are employed which retain all possible thickness.

Hides and skins are generally received by the tanner

in a partially dehydrated condition, that is, part of the water has been removed by salting or drying. The first operation is to trim off matter which will not make good leather. Packs of hides of known weight are then made up and soaked (generally overnight) in pits of clean, cold water. Soaking accomplishes three purposes: (1) the hide is rehydrated or reswollen nearly to its original condition; (2) the salt is dissolved; and (3) the dirt is loosened. Care must be taken that the time and temperature of soaking are such as to prevent bacterial action. In some cases, antiseptics are added to the soak to avoid this danger. The next chemical operation is the removal of hair. This is usually preceded by fleshing (a mechanical operation), carried out in a machine equipped with a multi-bladed radial knife which scrapes off residual flesh, leaving a uniform surface for the action of chemicals in subsequent operations. Figure 3 shows such a machine in operation.

It has been mentioned that hides and skins are made up of different proteins. Those of which the hair and grain are composed are known as keratins. These are much more affected by alkali than collagen, of which the corium or body of the leather is composed. In the removal of hair, hydrated lime (calcium hydroxide) has been employed for ages for this purpose. Lime has



Courtesy of A. C. Lawrence Leather Company

FIGURE 3.—FLESHING MACHINE

the advantages of limited solubility and not too harsh alkalinity, so that there is practically no danger of injuring hides by its use. Lime dissolves the cementing material from around the hair roots, permitting easy removal, as will be explained below. Further, the treatment plumps the fibers so that the skin is considerably swollen after liming. The third action is its combination with fats of the hides to form lime soaps. Since two or three days to a week's time is required for liming, it has become the practice to use supplementary or sharpening materials to hasten the action. Among these are sodium sulfide (Na_2S), and more recently, sodium and calcium sulfhydrides (NaHS or $Ca(HS)_2$).

Removal of hair is accomplished mechanically by the use of a machine similar to the fleshing machine, but with a dull knife. The hair, together with the cementing material, is squeezed out and removed by the knife, along with the lime soaps and dirt. After this operation the hide is translucent, cream colored, swollen, and rubbery. Up to this point, procedure is the same for practically all types of hides and skins. Since in subsequent operations so many variations are possible, we will confine our attention to treatment of chrome-tanned upper leather, which is typical of modern practice.

The next operation is chemical and is known as "bating." It has a twofold purpose: removal of some of the lime and of certain proteins on the grain of the hides. Materials commonly employed for these purposes are ammonium salts (chloride or sulfate) and pancreatic extract from animal glands. The ammonium salts dissolve the lime:

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_4OH$$

and bring the pH to the point at which the enzymes in the pancreatic extract are activated. These then attack the protein. During this operation the swelling is removed or, in trade terms, the hide "falls."

The hide is immediately transferred to a pickle bath consisting of sulfuric acid and common salt. The hide has an affinity for acid, actually taking up hydrochloric acid from this bath. It should be noted that the hide then becomes strongly acidic and swollen (although the purpose of the salt is to prevent undue swelling). Any residual lime is converted to calcium sulfate.

$$Ca(OH_2) + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$$

Pickling converts the hide into a white, soft state in which it can be kept for considerable periods. This is valuable in tannery practice as up to this point the hide would be ruined unless it were kept moving through the successive operations just detailed. It should be noted that pickled stock is not leather, in that if it is put into water it will gradually dissolve, while it will be recalled that leather is insoluble.

In the next operation the hide is tanned by chemical means. The hides are placed in wooden drums, which can be rotated on their axes. The tanning solution is fed through a hollow pipe in the axis. Typical drums are shown in Figure 4. A solution of basic chromium sulfate [$CrOH(SO_4)$] is employed. This solution is unstable and after it has become uniformly distributed through the hides the addition of a small percentage of sodium bicarbonate ($NaHCO_3$) causes the chromium

to combine chemically with the hide substance. At this point the hides become leather. The common way of testing the completeness of tanning is to place a piece of hide in a beaker of water. The water is then heated practically to the boiling point without appreciable curling of the hide. The significance of this test is that the chromium has combined with the hide substance, rendering it insoluble. If tanning is incomplete, chrome or other tanning material is extracted and the hide reverts to its raw state, curling up and becoming hard.

After washing to remove excess chromium salts, acid, etc., the hides are subjected to mechanical operations. First, they are split to the desired thickness. As explained earlier, the purpose of this operation is not to create two hides where one existed before, but rather to produce leather sufficiently thin and supple for today's needs. Splitting is accomplished by a very interesting machine, involving the use of a continuous or a band knife which is kept sharp by a grindstone rotating against it. The hide is forced against the edge of the knife and an elaborate system of rollers ensures the grain split of the proper thickness. Splitting can be performed in the limed condition if desired and this permits a different method of tanning to be used on the flesh split than on the grain split.

The next operation is shaving, to make sure that the grain split is of uniform thickness all over. In other words, this supplements the splitting operation. In the case of calfskins, which are not split, shaving is employed to remove some of the flesh portion from the heavier backbone area.

The hides are next returned to the drums and solutions of aniline dyes are added to color them to the desired shade. Sulfonated oils and fats are usually added during the same operation to lubricate the leather fibers.

Hides are then dried. Commonly they are conveyed through tunnel driers in which desired temperatures and humidities may be maintained. Proper drying conditions are essential to ensure uniformity of quality and drying time. Subsequently, hides are allowed to regain some moisture and are then staked. This operation consists in flexing the hide mechanically and results in rendering the hide uniformly soft to the desired degree. During the drying operation the individual fiber bundles have become cemented together. If properly conducted, the staking operation separates them so that they can slide on one another. The essential structure of fiber bundles, however, is retained, since leather depends on this for its unique properties.

Hides are next toggled or tacked on frames or boards and then redried. This operation produces hides which are flat and smooth on the grain.

They are now ready for the finishing operation which varies widely according to the purpose for which the leather is to be used. While for some years past finishes of casein, shellac, and pigments have been employed to produce the desired shade and texture, more recently synthetic resins or plastics have been used. Polyacrylate emulsions, polyvinylchloride, or urea-formaldehyde solutions are now used. The solutions are applied by spray, swab, or brushing machine. Two to six coats are required with intermediate drying.

Courtesy of A. C. Lawrence Leather Company

FIGURE 4.—TANNING IN WOODEN DRUMS

Following the application of the finish, leather is smooth plated if a lustrous, smooth surface is desired, or embossed to give a different texture. Thus, alligator, seal, or other grain appearances can be simulated. It should be emphasized that leather so treated is not misrepresented to the trade, being sold as alligator-grained cow hide, etc. These operations are carried out by placing the leather in large hydraulic presses. Under many tons pressure a heated plate of the desired surface pattern is pressed down on the grain of the leather. Further refinements in appearance may be obtained by the application of wax emulsions, or by glazing operations in which flint glass cylinders are used under great pressure to give the hide its luster.

Vegetable tanning agents are used on approximately half of the leather produced in this country. Extracts of barks, wood, shrubs, or seeds containing tannin are made by treating these materials with hot water, much in the way that coffee is made. After liming, treatment with lactic acid is usually given and vegetable extracts are applied. The vegetable tanning process, in general, requires a much longer time than chrome tanning and in the case of sole or heavy leathers it takes weeks for completion. As in the case of upper leathers, drying and supplementary finishing operations are required to produce leather of the desired characteristics.

LETTERS

Teaching and Tests

To the Editor:

T. B. Coolidge's[1] letter about his troubles in teaching elementary chemistry to medical students has interested me not only in its relation to premedical students but also as a statement on science teaching in general. In teaching general inorganic chemistry to college freshmen I, too, have found a surprisingly inadequate preparation for the study of science.

When I first met the lack of fundamental notions of even arithmetic and grade-school general science I was very much inclined to feel the same way about the high-school science teacher as Coolidge does about the college professor.

Discovering that some freshmen were unable to transform decimals into fractions or fractions into decimals, I gave a test of nine transformations of this kind (taken from a sixth grade textbook) to my class of 25 college freshmen. Only six of them answered all the questions correctly and two of them managed to miss them all. The rest had three to eight answers correct. The students had attended 11 different high schools and 15 different grammar schools. It is improbable that in all these schools students could graduate without having learned an elementary technic like this one. Moreover, one of the students with a complete failure came from the same high school as students with scores of better than 80 per cent.

These data, together with many observations in my classes, led me rather to believe that the unsatisfactory work of our students is less the failure of the particular teacher than of the educational system. The answers in this test, as in many other examinations, show clearly that the student is taught how to memorize, but not how to understand. Six of the students gave the transformations: $0.25 = {}^1/_4$; $0.66 = {}^2/_3$; $0.15 = {}^1/_6$ or ${}^1/_7$, memorized approximations, since they were unable to compute the values.

It seems to me that here is one root of the difficulty of teaching science. Our system of examinations lets the student get away with memorized material, whereas an understanding of the facts and principles involved ought to be required. The true-false or multiple-choice questions do not even require memory. The probability of guessing the correct answer is high. Prerequisite for the completion test is some memory, to be sure, but not very much. It is easier to insert the words "mol fraction" in the incomplete sentence: "The partial vapor pressure of a component in solution varies directly with ——" than to recite the whole law and to apply it sensibly. Many teachers are aware that a true-false test is absolutely insufficient for a science examination and supplement it with problems and descriptions, or else use such types of questions entirely. An essential improvement in the science education of our students will be achieved only when examinations are based entirely on descriptions and problems, in college and high school as well as in university courses.

The subdivision of the Coöperative Chemistry Test into the three groups: Information and Vocabulary, Problems and Equations, Scientific Method (quoted from Form 1938) is certainly a step in this direction. But it is only the first step, since even the problems are set up in the form of multiple choice, which leaves a 20 per cent probability of a correct answer by the ignorant student. Furthermore, there is no discrimination in evaluating an answer; each correct answer counts one point, for each erroneous one a point is deducted. But it is certainly a much more serious mistake to state, "hydrogen can be prepared by the reaction of a hot concentrated oxidizing acid" (question 2, answer 5, Form 1938) than to commit an error in answering any one of the questions of Part III on the scientific method. A step in the right direction might be the suggestion of Charles DeWitt[2] that the test be divided into two groups, of which the first will lead to a *C* grade only and which must be answered before undertaking the second part upon which higher grades are based.

In this Institute chemistry examinations are given in six groups: I. Laws, II. Equations, III. Calculations, IV. Manufacturing Processes, V. Application of Principles, VI. General Information. Each group comprises two to four questions. The student is asked to answer one question out of each group and then to select six additional questions from any group he prefers. The questions never contain true-false, multiple-choice, or completion questions and are so arranged that no more than three groups of questions may be answered by memorized material. Hence, students who rely on their memory only will have no chance of getting more than a *C* grade.

In this way it is possible to stress the necessity of certain fundamental notions. The system is not yet sufficient to reach the goal which Coolidge expects us to reach. As long as we stick to the idea that all questions are of equal importance it will frequently happen that a student misses a fundamental question like the definition of oxidation but answers all the other questions correctly and, hence, may get a good grade. Consequently, the teacher on the next higher educational level will be surprised what elementary things students were not taught before.

It seems to me that the way out of this dilemma is either to abandon the system of grading by the score or to devise a more adequate method of weighting questions, and also weighting the deductions for wrong answers, depending upon the seriousness of the error.

F. FROMM

POLYTECHNIC INSTITUTE OF PUERTO RICO
SAN GERMÁN, PUERTO RICO

[1] J. CHEM. EDUC., **19**, 143 (1942).

[2] DEWITT, "A grading system for general chemistry," J. CHEM. EDUC., **19**, 129 (1942).

Chemistry and World Problems

To the Editor:

The following is an answer by a high-school student to an unrehearsed question: "What has your beginning course in chemistry offered you for the solution of world problems?"

"(1) My chemistry has shown me that all nations have a need for raw materials located in many countries, not one.
(2) Chemistry has shown me that the world of tomorrow can be better if we wish to make it so, for
(3) The scientific method has shown me that some of our trouble lies in our way of thinking.
(4) My study has shown that science can and does work for the benefit of mankind if we wish it so.
(5) The famous figures of science have helped me to realize that there are great men among all the races."

I think we can say that this boy has grasped the principles of appreciation and understanding. Does he know the facts of chemistry? Oh my, yes!

GRETA OPPE

BALL HIGH SCHOOL
GALVESTON, TEXAS

A Rough but Brilliant Diamond

To the Editor:

I enjoyed very much reading Dr. Berl's article on "Some Personal Recollections of Alfred Werner" in the JOURNAL OF CHEMICAL EDUCATION, and, of course, I deeply appreciate the compliment of mentioning my name in connection with his.

I became very fond of Alfred Werner and got to know him extremely well because of the work which I did for him. Over a period of some nine years, a series of men in his laboratory had unsuccessfully tried to prove for him that there were optically active isomers that were not dependent on the asymmetry of carbon: so that when my work turned out successfully and the first optically active chemicals of this sort were prepared, he was immensely pleased.

While some people thought that he had a somewhat rough manner, it was the roughness of the uncut diamond and was counterbalanced by an extreme brilliance of thinking. I shall never forget the day that the optically active isomers were first attained. In connection with this work, I had been carrying out some 2000 fractional crystallizations and had been studying Madame Curie's work on radium for that purpose. After having made these 2000 separate fractional crystallizations which proved that the opposite ends of the system were precisely alike and that we had to do something more drastic, I proposed increasing the dissimilarity of the diastomers by using brom camphor sulfonic acid as a salt-forming constituent having extremely high optical activity. When this was tried, the isomers in the form of these salts literally fell apart.

Prior to this, almost everyone in academic circles, knowing the reputation of the problem, used to greet me on the streets in Zurich with the inquiry, "Well, does it rotate yet?" It got to be a standing greeting with which everyone met me; so when the day came and I walked into his office with the information, he leaned back in his chair, smiled, and said not a single word.

This was just before his main lecture at five o'clock in the evening, a lecture which was always so crowded that many people sat on the steps. When he didn't appear on his usual punctual minute, there was some commotion and finally a young student appeared at the door down at the bottom of the lecture hall and announced that the professor wanted to see me in my laboratory at once and that the lecture was canceled. Naturally, there was considerable astonishment. On rushing to my laboratory, I found Professor Werner already there, and it was then that his brilliance was so obvious. He scintillated in the work which followed as to what to do. He was fearsome lest we should lose the optical activity, fearsome that the materials might racemize overnight, etc. So we made many salts and many combinations until late at night. As it turned out, none of them ever racemized anyway, but it was extremely interesting to see his mind at work on an occasion of that sort. Also, we had a little race between my laboratory and his assistants to see who could get the material analyzed for complete elemental analysis first and verify that our accomplishments were unassailable. He came in to see me the next day, or the day after, inquiring, "Well, our analyses check, how about yours?" and I was able to say, "Mine checked yesterday."

We got along famously and I have always cherished a tremendous admiration for him and intensely appreciate the opportunity of having worked under his direction.

V. L. KING

TECHNICAL DIRECTOR
CALCO CHEMICAL DIVISION
AMERICAN CYANAMID COMPANY
BOUND BROOK, NEW JERSEY

The Gram Electron

To the Editor:

I should like to express my appreciation for the interesting contents of your JOURNAL. I particularly appreciate detailed writeups of interesting experiments for laboratory courses as the one in electrometric thermochemistry by Cameron and Wright.[1]

I was quite interested in the article, "The Gram Electron," by Audrieth and Copley,[2] and was on the point of writing a supplementary article. I think that the mol of electrons should play an important place in atomistics. I am a little concerned, however, with the large emphasis on the mass of the mol, and I am quite amused at the large diversity of symbols used in standard textbooks for one mol of electron, as I have been able to run across ten different symbols. As I pointed out in footnote 10, in a recent article [*J. Am. Chem. Soc.*, **64,** 398 (1942)] one can assign the following conven-

[1] CAMERON AND WRIGHT, "An experiment in electrical calorimetry," J. CHEM. EDUC., **18,** 510 (1941).
[2] AUDRIETH AND COPLEY, "The gram electron," *ibid.*, **18,** 373 (1941).

tional thermodynamic constants for the solvated electron: $\Delta F = 0$, $\Delta H = 0$, and $S = 15.6$ cal. per degree. I have always used the Lewis and Randall symbol E^- for the electron, but Professor Pauling suggests that it should not be given a capital letter symbol, since we do not conserve it as we do atoms, but it should be symbolized as by e^-, with the minus sign designated since we do use conservation of charge in balancing equations.

CHARLES D. CORYELL

UNIVERSITY OF CALIFORNIA
LOS ANGELES, CALIFORNIA

Out of the Editor's Basket

WE HAVE just received a copy of the third progress report of the Committee on Carbohydrate Nomenclature, representing three of the interested Divisions of the A. C. S. It is much too extensive to be digested here, but anyone interested may obtain a mimeographed copy from the secretary of the committee, Dr. H. S. Isbell, National Bureau of Standards, Washington, D. C.

● The following quotation from a recent number of *Silicate P's and Q's*, issued by the Philadelphia Quartz Company, may be of interest:

"The current necessity for protecting attic timbers from fire bombs has brought sodium silicate into the news. A British suggestion is a paint made by mixing twenty-four ounces of china clay with eighteen ounces of sodium silicate syrup in a pint of water. Other pigments can be substituted for the china clay. Silicate coatings of this sort are effective because they delay ignition by their insulating action. When the silicate film is heated it tends to intumesce or puff, through pressure of the steam developed by the water in the film. The puffed film has considerable insulating value and as long as the film is continuous it protects the wood from direct contact with the flame. Of course on long exposure to high heat the wood begins to distill, and the gases, when they finally break through, will ignite, but such silicate films are very helpful in preventing ignition from sparks or short-lived flames."

● During World War I we worried about "the Nitrogen Problem." Now we have the answer to that, but this time it is "the Rubber Situation" which we hear about from all sides. Among the good summaries of this situation is the one in a recent number of *Fortune*. Mr. John L. Collyer, president of the B. F. Goodrich Company, recently pointed out the principal factors, which are probably already well known to most of us. We must rush the building of synthetic plants without losing a moment. Two other equally big jobs are the collection of scrap rubber for reclamation and the better conservation of the supply we already have. The setting out of new plantations and the development of new sources of natural rubber, such as guayule, will also be of importance in the long run, but the pressing problem is the immediate one.

Those who have observed in the public press the attacks which have been made upon the Standard Oil Company, for the reputed delay which its foreign relations are said to have caused in the development of synthetic rubber production, will have wondered if there may not be two sides to the question. An excellent summary of the *other* side of the question is found in the May number of *Esso Oilways*, issued by the Standard Oil Company of New Jersey from its Editorial Office, Room 1561, 26 Broadway, New York City. The summary is in question and answer form and discusses some of the evidence brought before the Truman Committee of the U. S. Senate. The one question uppermost in the public mind was disposed of as follows:

"*Question:* Did Standard Oil violate any law by making agreements for exchange of information with I. G.?

"*Answer:* No, and no such charge has ever been made by any responsible person. It has been common practice for American companies to make agreements with foreign companies by which the fruits of scientific development throughout the world could be brought to the United States. The question of legality, however, hinges entirely upon the detailed patent problems which grow out of such exchanges. Regardless of this question, upon which there are sharp differences of opinion, the United States at the beginning of this war was in a much stronger position in terms of chemical resources than at the beginning of the last war—simply by virtue of American enterprise which combed the world for scientific knowledge. When we entered the first World War many foreign companies, notably those in Germany, held monopolies on developments and processes which we needed, but from which we were cut off. That could not happen this time. Referring specifically to rubber, we 'brought home the bacon.' Some quarrel with the way it was wrapped up. Nevertheless, it is here, and it is under American, not German, control."

● We clipped the following from *New York State Education*, contributed by John Conway, a senior, of the Freeport High School:

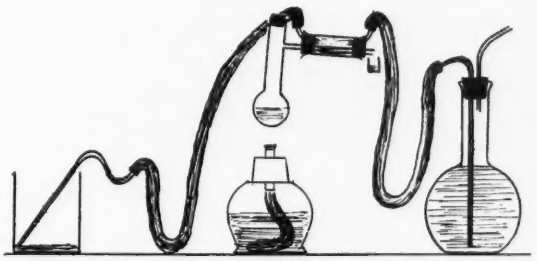
"The entry of the United States into the second great World War has opened the way for many of our high school youth to become of service to their country. As many of our young men are being drafted to defend our country, they will leave jobs which are vital to everyday civilian life. There will also be many new jobs created by our expanding defense industries, all of which the youth of America will have to fill. American youth will be called upon to aid our defense effort in many ways. . . .

"Throughout the United States about 30,000 students, members of science and engineering clubs, are staying after school to tackle research problems. Many of these problems have proved too difficult or haven't even occurred to other men. Some of these students have already made contributions to our technical industries. One student has succeeded in developing a palm-sized radio that both sends and receives messages. This radio has already been accepted by the Army. . . .

"Though many of our recent and prospective high school graduates will not be able to participate directly in the defense effort, they will aid it by going through college in three years instead of four. As there will be a demand for leaders in our nation's fight two or three years from now, it is necessary that students be

trained in leadership. These students will supply fresh blood to our war effort. American students can best aid in preserving democracy by continuing their educations."

● The accompanying illustration of a portable water still, for use with a microchemistry set,[1] was sent in



PORTABLE STILL

by E. Edward Johnson, of Omaha, Nebraska. It makes use of a 125-ml. wash bottle and a 10-ml. distilling flask. The short condenser built around the arm of the distilling flask operates by siphon action from the wash bottle.

● We have been urged to call attention again to the activities of the Division's Committee on Examinations and Tests. In view of the extra demand which war work makes upon your time, you may find it especially convenient to make use of the various prepared tests which are now available, rather than take the usual laborious pains to prepare your own. The tests in general chemistry and qualitative analysis, issued by the Co-operative Test Service (15 Amsterdam Avenue, New York City), have been frequently described in the JOURNAL. There are also available 27 topic examinations in organic chemistry (from Professor Ed. F. Degering, Purdue University, Lafayette, Indiana). These are accompanied by validity data, so that you may select the more valid items for short quizzes.

● A National Registry of Rare Chemicals has been organized by the Armour Research Foundation, which is located at and affiliated with the Illinois Institute of Technology, and is now ready to begin regular operation.

Information on chemicals too rare to be listed in the catalogs of regular chemical supply houses will be filed with the Registry and indexed according to name, location, and amount available. Dr. Martin H. Heeren, chairman of chemical engineering research in the Foundation, will direct this work and has been named director of the Registry.

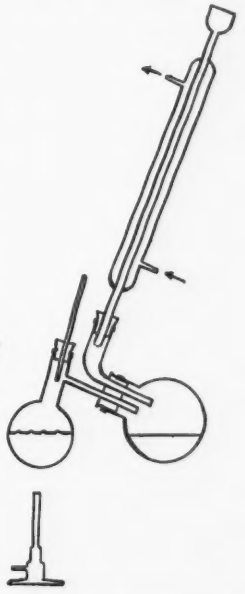
Throughout the country's laboratories, schools, and industrial plants exist uncommon chemicals made for a highly specialized market and not generally known to exist, Dr. Heeren says, but which are constantly needed by research.

The Registry is not a "chemical bank," inasmuch as it does not store the actual chemicals. It does not buy or sell them, but merely maintains an indexed file of their sources and supplies.

● Albert C. Holler, of the United States Metal Products Company, Erie, Pennsylvania, describes the construction of an automatic wash bottle in which he uses a one-way, ball type valve in the rubber mouthpiece. These valves, used in nasal atomizers and bulbs, can be obtained at any drug store. The three-holed rubber stopper is provided with the common short glass tube, open at both ends, which can be kept closed with the thumb during the use of the bottle and opened to release the pressure and prevent dripping. The valve in the mouthpiece prevents the escape of pressure on removing the bottle from the mouth, while the bottle continues to deliver until the thumb is raised and the pressure released.

● "Ultraviolet in Science and Industry" is published by Alpine Press, Newark, New Jersey (50 cents), and contains interesting and useful information about the development and use of quartz lamps and the general application of ultra-violet light in chemical analysis, inspection of documents, crime detection, biochemistry, and industry in general.

● The modified distillation apparatus, shown in the illustration, was devised by Herman S. Levine, of the Erie Center of the University of Pittsburgh, for special use with low-boiling liquids such as ether, CS_2, etc.



DISTILLATION APPARATUS

● Benjamin J. Novak, of the Murrell Dobbins Vocational School, Philadelphia, undertook to determine the amount of space in the *New York Times* devoted to science. The years 1930, 1933, 1936, and 1939 were covered completely, 75,000 pages in 1461 issues. The amount of space devoted to science was found to be 52,238 column-inches (nearly 10 miles!) of which 4969 inches, or 9.5 per cent, were devoted to chemistry. Certain closely allied branches such as atomic physics and radioactivity represented an additional 1500 column-inches. The greatest amount of space was taken by health and medicine, 20.1 per cent. He observed that the percentage of chemistry in the newspaper science increased from 7.4 per cent in 1930

[1] J.CHEM. EDUC., **19**, 145–6 (Mar., 1942).

to 16.0 per cent in 1939. The attention given to organic chemistry increased the most during this time —more than threefold, in fact. About two-thirds of the space was given to "applied" chemistry; the rest could be characterized as "general principles."

A significant conclusion, of interest to the teacher, is that a rather substantial knowledge of general principles is assumed on the part of the reader.

● The National Safety Council has issued a 1942 printing of its safe practices pamphlet No. 60, entitled "Chemical Laboratories." This twelve-page folder covers thoroughly the field of safe and recommended practices dealing with chemical equipment, apparatus, and other matters in the experience of the chemical laboratory worker. Topics mentioned include design of laboratories, ventilation, illumination, drains, furniture, housekeeping, storage of chemicals and apparatus, fire protection, compressed gas cylinders, labeling bottles, opening bottles, glass tubing connections, desiccators, pipets, acid analysis, nitrometer, drying samples, volatile flammable liquids, personal protective equipment, pressure work, refuse disposal, first aid, and miscellaneous recommendations.

Single copies of this pamphlet are available to nonmembers of the Council at 25 cents per copy from the Council's office at 20 North Wacker Drive, Chicago, Illinois.

FROM SNOWFLAKES TO METAL SURFACES

BECAUSE Vincent J. Schaefer, of the General Electric Research Laboratory, made a hobby of collecting plastic replicas of snowflakes, scientists now have a simple method of observing details of metal structure far too fine to be seen with the ordinary microscope. Since these metals are vital in the construction of essential parts of airplanes, guns, warships, and tanks, any observations which can tell more about them, and possibly how to make them stronger and better, are of tremendous importance.

Ordinary microscopes, using light, magnify at the most some 2500 diameters. By using the new electron microscope, however, as much as 50 times the magnification of the best enlargements in light microscopes can be made. The image is visible on a fluorescent screen, which shines where the electrons strike. Or the images may be recorded on a photographic plate.

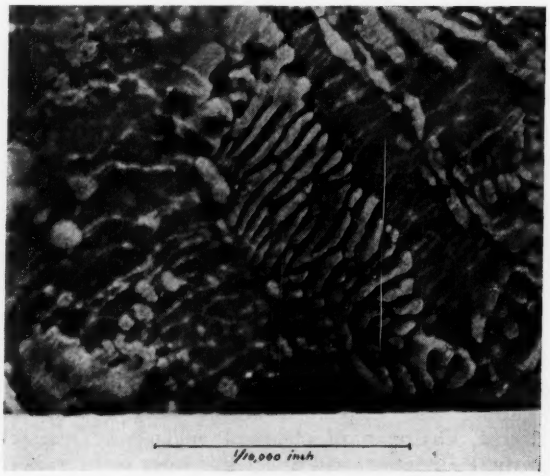
Electrons have little penetrating power, so the entire microscope must be exhausted of air. Also, the specimen being magnified must be very thin, otherwise the beam cannot get through. Unfortunately, samples of metal cannot be made thin enough to be examined in this way.

Complicated methods have been devised to eliminate this difficulty. One is to evaporate on the metal sample in a vacuum a thin film of silver, and to reinforce this film by plating on the back another metal, like copper, so it can be stripped away. Then a very thin film of collodion is flowed over the silver and, after hardening, the whole silver-collodion-copper assembly is immersed in nitric acid. The silver and copper are dissolved away, but the collodion remains, a faithful replica of the original surface that can be examined in the electron beam. Experimenters who developed this method reported trying to strip a thin plastic film directly from the metal, but without particular success.

However, Mr. Schaefer, who has been associated for a number of years with Dr. Irving Langmuir in his work on thin films, had been reproducing minute details of snow and frost crystals by "casting" them in a film of Formvar. As a hobby, he has made a large collection of such crystal replicas, obtained during winter snowstorms, formed on glass on cold nights, or even made in the ice box in summertime. Our frontispiece shows one of these snowflake "casts," in an ordinary microscope. Before the electron microscope was introduced he had also made strippings from metal surfaces. Consequently, when an electron microscope was installed in the General Electric Research Laboratory, Dr. David Harker, who has charge of it, turned to Mr. Schaefer for assistance.

After some experimentation, he found why it had been difficult to get good films directly. Even with the most careful cleaning, a few grease molecules will soon settle on the surface, and these interfere with the removal of the film. This was overcome by cleaning the surface immediately before the film-forming material is applied. This consists of a solution of Formvar, a plastic, in dioxane, a commercial solvent. After the dioxane evaporates, the specimen is immersed in water, and the Formvar film, only a half-millionth of an inch in thickness, is stripped away. Less than five minutes after the specimen is received from the polishing room, it can be examined in the electron microscope.

High places on the metal are thin spots on the Formvar film, while valleys come out as thick places. These scatter the electrons more, and appear darker in the final image. This is also the way the specimens appear in the usual metallographic microscope, where high spots are light, and valleys dark. Metallurgists accustomed to light photographs find that they can easily interpret the electron images, and report that there is a fascinating new field of unexplored possibilities here.



A METAL SAMPLE, SHOWN IN AN ELECTRON MICROGRAPH, WITH MANY TIMES THE MAGNIFICATION OF THE BEST PHOTOMICROGRAPH MADE WITH THE OPTICAL MICROSCOPE

Fine details of the metal's structure never seen before are here revealed.

RECENT BOOKS

THE CONDENSED CHEMICAL DICTIONARY. Compiled and edited by the editorial staff of the Chemical Engineering Catalog (*Francis M. Turner*, Editorial Director). Third Edition, completely revised and enlarged under the supervision of *Thomas C. Gregory*, Editor. Reinhold Publishing Corporation, New York City, 1942. 756 pp. 15 × 23 cm. $12.00.

This third edition of a standard work which has already found an important place in the chemical literature contains a number of new features. Among these is the inclusion of a large number of chemical specialties which are sold under trade or brand names. In many cases there are also "typical specifications" which describe the product as marketed and sold commercially. Over 6000 new items have been added in this edition.

Anyone not already familiar with the DICTIONARY will find in it a surprising amount of useful information about many substances or products with which he may have to deal. In a few cases this information is quite extensive and encyclopedic. More than four pages are devoted, for example, to the subject of vitamins. An interesting table shows the effect of wartime on chemical prices.

The sixty-page appendix contains miscellaneous tables which will prove useful, but which will scarcely be a substitute for a good handbook. The DICTIONARY should be on the reference shelf of every well-equipped laboratory.

NORRIS W. RAKESTRAW

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WORKING WITH THE MICROSCOPE. *Julian D. Corrington*, Ph.D., Professor of Biology, Washington College, Chestertown, Maryland; Editor, Microscope Department, *Nature Magazine;* Permanent Secretary, American Society of Amateur Microscopists. Whittlesey House (McGraw-Hill Book Company, Inc., New York City and London, 1941). xi + 418 pp. 121 figs. 15 × 23 cm. $3.50.

"Designed as a complete guide and reference work for those who wish to learn microscopy and micro-technic, this book not only tells the beginner how to use the instrument itself but gives complete instructions on the preparation of slides, or specimens, of every degree of difficulty from the simplest to the highly technical." Practically every type of subject and field of interest is treated; every process is explained in clear, simple language. By following these practical directions, the amateur can learn microscope technic by himself, step by step, without outside help. In addition to the material on the preparation of slides, the book contains useful information about the microscope and its accessories, new methods in microscopy, short cuts, and special problems. The material is well organized and attractively put together. Full directions on the preparation and use of reagents, a list of sources of supplies, a bibliography, and reference tables are included.

The book will be of interest to every amateur, hobbyist, and student—anyone except the advanced professional—who wants to learn something of the science of microscopy.

MODERN PULP AND PAPER MAKING. A PRACTICAL TREATISE. *G. S. Witham, Sr.* Second Edition. Reinhold Publishing Corporation, New York City, 1942. 705 pp. 319 figs. 15 × 23 cm. $6.75.

This volume is intended as a practical treatise rather than a scholarly work, and as such has a more direct appeal to the man working in mills located far from any reference library. The first edition was published in 1920 and represented thirty-seven years' experience on the part of the author; the revision brings an additional fifteen years of active work in mills in various parts of the United States and Canada. After the author's death, this revision was published from his manuscript with the collaboration of his son, George S. Witham, Jr.

The present volume presents the practical side of pulp and paper manufacture much more adequately than the usual textbooks on the subject. This is especially true of the chapters on the saw mill and the wood room. It is also reflected in the series of specifications which are given for various types of machinery used by the industry, in the lists of equipment for a groundwood mill and a sulfite mill, the table of power requirements for the various units, the discussion of personnel and records, etc. However, many tables of data have been omitted because they can be found in the Paper and Pulp Mill Catalog. The scope of the book is indicated by the chapter headings: Processes by Which Pulp Is Produced; Materials of Pulp; Varieties of Paper; The Saw Mill; The Wood Room; Sulphite Mill; The Acid Plant; The Alkaline Processes; The Groundwood Mill; Screening and Refining of Pulp; Bleaching; The Beater Room; The Machine Room; The Finishing Room; Converting and Coating; Paper Defects: Their Cause and Cure; General Design of Pulp and Paper Plants; Personnel and Records; The Power Plant; Testing of Paper and Paper Materials.

Unlike many books which are now produced as the result of the coöperative efforts of a number of experts, this work is the product of one man's time and thought. Therefore, it may be expected that certain subjects may not be completely covered, but the author's broad experience would suggest that, in general, we have a reliable, practical guide to the industry.

From the viewpoint of education, this book should be considered as a very valuable supplement to the ordinary textbooks in that, as mentioned above, it supplies the practical aspect of the industry. It will be of particular interest to the young technicians and operators, because it gives them a comprehensive insight into the industry in which they are engaged or which they may contemplate as a future source of employment.

CLARENCE J. WEST

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MODERN PLYWOOD. *Thomas D. Perry.* First Edition. Pitman Publishing Corporation, New York City, 1942. xiii + 366 pp. 129 figs. 15 × 23 cm. $4.50.

A complete manual of plywood from its early history in ancient Egypt to the modern technics making use of synthetic resin adhesives. The book discusses all the uses of plywood, the various adhesives, the methods of manufacture, and the machinery involved. The first section is a glossary of terms and the last is a reasonably complete bibliography. Three sections before the last one present valuable tabular data of a technical sort, grading rules, and methods of testing for adhesive strength. The treatment is authoritative, the presentation is logical, and the text is readable. The book will be valuable to individuals in many fields and perhaps suggestive to those in non-wood-using industries, but it will contribute very little to chemical education.

WALTER H. SNELL

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PROVIDENCE, RHODE ISLAND

GENERAL CHEMISTRY EXPERIMENTS. *R. D. Billinger*, Ph.D., and *Hilton A. Smith*, Ph.D., Lehigh University. Second Edition. Times Publishing Company, Bethlehem, Pennsylvania, 1941. ix + 307 pp. 28 figs. 14.5 × 22.5 cm. $2.25.

For each experiment, this laboratory manual gives a short discussion of the theoretical background, directions for procedure, and illustrations where advisable. Detachable data sheets provide spaces for the date, name of student, and desk number; observations are to be filled in, and equations for reactions are to be written. Each experiment has a number of related questions to be answered in the blank spaces provided. The laboratory manual is thus compact, uniform, and well organized throughout. The 69 experiments offer a variety from which the instructor can choose those suited to his purpose.

TEXTBOOK OF QUANTITATIVE ANALYSIS. *William Thomas Hall*, Professor Emeritus of Analytical Chemistry, Massachusetts Institute of Technology. Third Edition. John Wiley and Sons, Inc., New York City, 1941. xiv + 364 pp. 51 figs. 15 × 23 cm. $3.00.

The first edition (1930) was largely an adaptation of the large Treadwell-Hall to the needs of students in a one-year beginning course at M. I. T. This present edition is considerably revised in the light of ten years of use in that course. Part one contains the introductory work on volumetric analysis, acidimetry and oxidimetry, including the use of ceric salts, gravimetric determinations of chlorine, iron, and sulfur, phosphoric acid, and the analysis of cement and brass. In the second part silicates, steel and ores are the principal subjects, and there is a chapter on potentiometric titrations.

There are many practical suggestions included to aid the teacher in the choice of laboratory exercises among the many methods described, as well as interesting comments on the author's own technic of grading and instruction. Numerous problems are included. The reviewer is repelled by the use of the term "polarity" instead of "polar number" or "oxidation number." "The polarity of an element is the sum of the positive and negative valence bonds which it has in a compound; it represents the state of oxidation. Usually the polarity is the same as the valence . . . but sometimes there is a difference. Nitrogen in the ammonium radical has a valence of 5, ... The polarity . . . is −3" (page 37).

In the chapter on acidimetry and alkalimetry is a badly drawn figure of three titration curves (unnumbered, page 49) which is repeated as Figure 49 on page 322. From this figure an observing student might conclude that 0.1 *N* acetic acid has a pH of 2.4 if you intend to titrate it with NaOH, but a pH of over 4 if you expect to use ammonia for the titration! The HCl curve is also badly drawn.

In the footnote on page 227 "mercuric" is written instead of "potassium." On page 319 the choice of a *tenth-normal* calomel electrode for illustration seems odd. The quinhydrone electrode is referred to as "the hydroquinone electrode," and the author speaks of "the 0.1 *N* calomel solution." The detailed directions for the preparation of quinhydrone are not so useful as they would have been before it was commonly marketed.

Of the many excellent features of the book the reviewer particularly liked the practical suggestions on manipulation, apparatus, and technic found throughout, the choice of methods of steel and ore analysis, and the elusive flavor of being a reference book which is being used as a text. This flavor is hard to describe, but must prove stimulating to the interested student. It is a carry-over from the large book by Treadwell and the author. The book should find many users in the more thorough college courses in quantitative analysis.

NORRIS F. HALL

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ORGANIC ANALYTICAL REAGENTS. *John H. Yoe*, University of Virginia, and *Landon H. Sarver*, American Viscose Corporation. John Wiley and Sons, Inc., New York City, 1941. ix + 339 pp. 2 figs. 15 × 23 cm. $4.00.

The use of organic reagents in analytical chemistry has increased markedly in the past few years. The authors of ORGANIC ANALYTICAL REAGENTS have rendered a valuable service by compiling information available in the literature as well as from their own exhaustive studies in the field. Unlike most texts, this one is not merely a compilation of data, but provides an attempt to correlate the structure of organic reagents with their reactions and uses in analytical chemistry. Without question this type of approach to the problem will serve as a stimulus to further investigations in the field.

The book is divided into two parts. The first part is concerned primarily with descriptive and theoretical material, while the second part contains a very complete list of organic compounds used for the detection or determination of a number of elements. More than 2400 references are included, and cover the literature to July, 1940.

Part I includes the following topics: Classification of Organic Analytical Reagents, Organic Solvents and Wash Liquids, Organic Acids and Bases, Oxidizing and Reducing Agents, Indicators, Primary Standards in Volumetric Analysis, Valence and Complex Compounds, The Salinogenic Reagents, Photometric Aids, and Miscellaneous Organic Reagents. Part II contains a list of hundreds of organic reagents used for the detection or determination of sixty elements, in addition to the rare earth elements. In certain cases a distinction is made in regard to the different oxidation states of the element in question.

The book is very well arranged, and information concerning a given reagent and element may be easily located. Structural formulas frequently are used and are represented clearly. This book will be well received by chemists interested in analytical chemistry. It should be available in all chemical libraries as a reference text.

WARREN C. JOHNSON

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INTRODUCTION TO CHEMICAL THERMODYNAMICS. *Luke E. Steiner*, Associate Professor of Chemistry, Oberlin College. First Edition. McGraw-Hill Book Company, Inc., New York City and London, 1941. xiv + 516 pp. 38 figs. 15 × 23 cm. $4.00.

"The first objective of this book is . . . to acquaint the student with . . . fundamental theory. A second objective is to prepare the student to utilize . . . the data found in the current chemical literature. A third . . . is to give the student a sound background for more extended work . . . ."

The author has fulfilled his purpose abundantly. The book is eminently teachable and should appeal to any student, yet there has been no sacrifice of rigor. The section on thermometry and the chapters on "Some Applications of Thermodynamics" and "General Equilibrium Conditions" are especially good. Most helpful is the inclusion of a discussion on empirical equations and limits of application of significant figures and units. Although the thermodynamic interpretation of spectroscopic data has had to be omitted, there is a good discussion of the elementary Debye-Hückel theory. The author is to be commended because he does not hesitate to use kinetics to illuminate thermodynamic equations.

It is surprising that there is no mention of osmotic pressure. Also the use of an equilibrium box and ideal gases seems a clumsy mode of derivation of the reaction isotherm compared to the use of activities. It is regrettable that the use of the fugacity concept has not been stressed in deriving the various solution equations, etc. The method is too simple and general to be disregarded.

The book contains 44 tables of useful data and an appendix of 4 tables of accepted constants, etc. There is a compilation of symbols used throughout the book. It is gratifying that the author has not found it necessary to depart from accepted usage in this respect. References are very numerous and plenty of problems terminate each chapter. Typographically, the book meets the high standard of the International Chemical Series.

This book is recommended to all teachers of the subject without reservation.

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IRON MEN AND THEIR DOGS. *Ferdinand C. Latrobe.* Ivan R. Drechsler, Baltimore, 1941. xiii + 225 pp. 139 figs. 16.1 × 23.9 cm.

A history of the growth and development of an American industry from Hayward and Friend, Stovemakers, to the Koppers Company, Bartlett-Hayward Division, Engineers, Manufacturers and Constructors—under the talisman of two cast-iron replicas of the primogenitors of the Chesapeake Bay Dog.